Development of Novel Methods of Analysis for Indoor Air Pollutants

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Abstract

The current variability and speciation of indoor VOCs are studied by analysing indoor air in UK homes and offices. These measurements were carried out via passive sampling into silica-treated canisters followed by thermal desorption-gas chromatography and high mass accuracy time-of-flight mass spectrometry (TD-GC-Q-TOF/MS). It was found that majority of the homes had d-limonene and α-pinene as the most abundant VOCs, with average concentrations ranging from 18 µg m^{-3} to over 1400 µg m^{-3} and 2 µg m^{-3} to 230 µg m^{-3} respectively.

In these analyses, cyclic volatile methyl siloxanes (cVMS) were frequently detected in high abundances. cVMS are chemicals in high volume production as they are used as solvents in formulations of consumer products. They were found in persistently high background concentrations in our analyses. Hence, a passive sampling method involving sorbents was developed to allow the analysis and quantification of these compounds, with LODs calculated to be 7.2 to 16.8 ng m^{-3}. This method was validated with real indoor air sampling with average D_5 and D_6 concentrations of about 2480 ng m^{-3} and 664 ng m^{-3} respectively.

Advancements have also been made in the development of a multispecies sensor for the detection of VOCs. A temperature control method was developed using a Peltier device and a control software programme written in LABVIEW. Attempts were made to manufacture a lab-on-a-chip GC column, but was deemed unsuitable due to leakage and mechanical problems. Instead, a short length of column was wound and placed in a copper enclosure. Tests were conducted using photoionsation detector (PID) as the detection method in this sensor development. The final set-up involved the assembly of the temperature control method, the GC column enclosure and the PID for the detection. Tests were conducted by introducing headspace standards into the set-up, with promising results.

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Author's Declaration

The candidate confirms that the work submitted in this thesis is her own and that appropriate credit has been given where reference has been made to the work of others. This work has not previously been presented for an award at this, or any other, University. All sources are acknowledged as references.

Parts of chapters 1, 2 and 5 have been published in scientific journals and conference publications with references as below.

C. M. Wang, B. M. Barratt, N. Carslaw, A. Doutsi, R. E. Dunmore, M. W. Ward and A. C. Lewis, Unexpectedly high concentrations of monoterpenes in a study of UK homes, *Environ. Sci.: Processes Impacts*, 2017, DOI: 10.1039/C6EM00569A.

C. M. Wang, B. D. Esse, A. C. Lewis, Low-cost multispecies air quality sensor, *Air Pollution XXIII*, *WIT Transactions on Ecology and The Environment*, WIT Press, 2015, DOI: 10.2495/AIR150091.

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List of abbreviations

cVMS	Cyclic Volatile Methyl Siloxanes
D_3	Hexamethylcyclotrisiloxane
D_4	Octamethylcyclotetrasiloxane
D_5	Decamethylcyclopentasiloxane
D_6	Dodecamethylcyclohexasiloxane
DCM	Dichloromethane
ENV+	Hydroxylated polystyrene-divinylbenzene copolymer
GC	Gas Chromatography
LOC	Lab-on-a-chip
M4Q	Tetrakis(trimethylsiloxy)silane
MS	Mass Spectrometry
PID	Photoionisation Detector
TD	Thermal Desorption
TOF/MS	Time-of-flight Mass Spectrometry
VOC	Volatile Organic Compounds

Chapter 1

Introduction

1.1 Volatile organic compounds

Volatile organic compounds (VOCs) are organic compounds with boiling points of less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa [1]. These compounds can have both direct and indirect impacts on human health; VOCs contribute to the formation of photochemical smog and ground level ozone [2-4] and some VOCs, e.g. benzene and formaldehyde, are considered to be carcinogens [2, 5-7]. VOCs are emitted from natural and anthropogenic (man-made) sources. Some natural sources of VOCs include vegetation, forest fires, and animals and these dominate the global budget of emissions [8]. Although on a global scale VOC emissions are largely from natural sources, air quality problems in populated and industrialized areas are mainly a result of anthropogenic sources [9]. Some examples of anthropogenic VOCs include tobacco smoke, biomass burning from human activities i.e. to exploit land for agricultural activities or to rid of agricultural waste, the production, storage and use of fossil fuels, and the production and use of household chemicals such as cleaning agents, coatings and paints.

In the troposphere, ozone formation occurs when ozone precursors react in the presence of sunlight (see Figure 1-1). The ozone precursors are nitrogen oxides and VOCs. VOCs contribute to the production of ozone, a constituent of photochemical smog that causes adverse health problems and also, when degraded in air, to the formation of organic aerosols. Ozone is formed in the atmosphere via a photochemical process whereby VOCs react with hydroxyl radicals in the presence of sunlight forming short-lived peroxy radical species (RO_2). RO_2 can then react further rapidly converting NO to NO_2, perturbing the natural photostationary state. Photolysis of the NO_2 formed then induces additional ozone formation. Ground level ozone is a secondary pollutant and a harmful photochemical oxidant which inhabits that troposphere, and is the main

component of photochemical smog [10]. Photolysis of ozone occurs with the absorption of solar ultraviolet radiation of wavelength shorter than 320 nm, resulting in excited O (^{1}D) atoms which have sufficient energy to react with water vapour to produce hydroxyl radicals.

$$VOC + OH \xrightarrow{[O_2]} RO_2 + H_2O \quad \text{(Rate determining step)} \qquad (1)$$

$$RO_2 + NO \xrightarrow{[O_2]} \text{Secondary VOC} + HO_2 + NO_2 \qquad (2)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (3)$$

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O\ \text{(Ground state)} \qquad (4)$$

$$O + O_2 \rightarrow O_3 \qquad (5)$$

$$O_3 + h\nu\ (\lambda < 320\ \text{nm}) \rightarrow O_2 + O(^1D)\ \text{(Excited state)} \qquad (6)$$

$$O(^1D) + H_2O \rightarrow 2OH + O_2 \qquad (7)$$

Figure 1-1. Ozone formation in the troposphere.

Ground level ozone is notably important when it comes to public health. Ozone when inhaled can cause serious health problems such as breathing difficulty, inflammation of airways, declination of respiratory and pulmonary function and aggravation of lung diseases [11, 12]. Exposure to ozone has also been associated with respiratory morbidity and mortality [13-16], some populations, i.e. the elderly and people with chronic conditions, being putatively more susceptible to ozone exposure [17, 18].

Ozone can be produced from simple hydrocarbons such as ethane, propane or from oxygenated compounds like formaldehyde and acetaldehyde. In indoor microenvironments and urban air, formaldehyde mixing ratios can vary from 1 to 100 ppb, while in remote clean oceanic areas formaldehyde is generally in the

range 0.1 – 1.0 ppb [19]. Ethane and propane originate substantially from anthropogenic pollution sources and have relatively long lifetimes against photochemical destruction. Background tropospheric mixing ratios of ethane and propane are 0.3 – 2.5 ppbv and 0.01 – 1.0 ppbv respectively. In addition to the production of ozone, acetaldehyde is also a precursor to peroxyacetyl nitrate (PAN), a secondary pollutant found in photochemical smog. It is a lachrymator and causes eye irritation. It has been reported that mixing ratios of PAN in clean air are typically 2 – 100 pptv, whereas that of polluted air can be as high as 35 ppbv [20]. Other anthropogenic sources of VOCs include fuel combustion, emissions from motor vehicles and evaporation of solvents and fuels [4] such as ethene, toluene and benzene [21, 22]. There are also biogenic sources of VOCs such as the emissions of isoprene and terpenes from plants [23, 24] that can also be important in the formation of ozone. The rapid and sensitive measurements of VOCs in ambient and indoor environments are therefore of great utility to environmental toxicology and atmospheric chemistry.

1.2 Indoor air quality

The quality of air in the indoor environment in which we live and work has been gaining more attention and awareness because of its importance to the health and well-being of occupants [25]. People in Europe spend at least 90% of their time indoors [26] making this on a time weighted basis the dominant environment for exposure. Two thirds of time indoors is spent at home, rendering the home environment a key setting for potential human exposure to air pollution [27]. The quality of air in the indoor environment is dependent on different factors such as the quality of the outdoor air, the building's design and location, air change rates, furniture within the building, and the behavioural habits of the occupants [28].

While an important source of indoor air pollution is the air from outdoors, it is noted that pollutants could be also generated from indoor sources. In addition to the natural sources (such as from animals, moulds, plants and flowers) of indoor air pollution, there is a large number of anthropogenic sources as well i.e. smoking of cigarettes, burning of candles, cooking and cleaning activities, emissions from building material and paints, and usage of personal care products [28]. Table 1.1 shows a list of indoor sources of pollution and some key indoor pollutants [28, 29].

The potential health impacts as a result of exposure to compounds such as those listed in Table 1.1 have been discussed previously [30, 31]. For instance, exposure to formaldehyde can cause sensory and airway irritation, asthma and cancer; house dust mites, fungi and bacteria may cause asthma and produce allergic reactions in some people; NO_2 increases susceptibility to infection, and therefore is a potential hazard of respiratory illness. VOCs generally cover a wide range of compounds, some of which are known to have harmful effects on human health i.e. benzene [6] and formaldehyde [32], both of which have been classified as carcinogenic to

humans by the International Agency for Research on Cancer [5, 33]. New complex substances could also be formed from the reaction between VOCs and oxidising compounds such as ozone [28].

Table 1.1. List of indoor pollutants and their sources.

Indoor sources	**Pollutants**
Natural	
Plants/flowers	Pollen
Animals (pets)	Biological allergens
Moulds	Biological allergens
Dust mites and insects	Biological allergens
Anthropogenic	
Air fresheners	VOCs
Personal care products	VOCs
Cleaning products	VOCs
Furniture, glues, insulation, carpets, cushions	Formaldehyde, VOCs, dust mites
Heating and cooking appliances	Particulates, nitrogen oxides, carbon monoxide, polycyclic aromatic hydrocarbons (PAHs), VOCs, ozone
Building and insulation material	Mineral dusts and fibres e.g. asbestos
Cigarette smoke	Environmental tobacco smoke including particulates, benzene and carbon monoxide

1.2.1 VOCs in the indoor environment

Indoor pollutants include volatile organic compounds (VOCs), some of which have both short and long-term adverse health effects and which are directly classified as toxic or carcinogenic [34-37]. VOCs are ubiquitous in any built environment but there is considerable variation in speciation and abundance. These variation of VOCs found in homes depend on many factors such as emissions, ventilation and the oxidative environment and these are evolving over time, reflecting changes in chemical use, behaviour and building design/materials. Sources of indoor VOCs include ingress of outdoor pollution from traffic and industry, outgassing from building materials, flooring, electronic equipment and furnishings, emissions from food, cooking, cleaning products, personal care products, and from people and pets [26, 38, 39]. Concentrations and speciation of VOCs in the indoor environment can also be influenced by seasonality, duration of occupancy, personal activities such as smoking and showering, and even the education levels of the occupants [40-42]. A list of some of the commonly detected indoor VOCs and their possible sources is shown in Table 1.2.

Table 1.2. List of commonly detected indoor VOCs and their possible sources.

VOCs	Sources
Alkanes, alkenes	
Isoprene	Plants, human breath
Hexane	Adhesives, aerosols in perfumes, gasoline
Cyclohexane	Paints, thinners, adhesives
Aromatics	
Benzene	Cigarette smoke, stored fuels, car exhausts
Toluene	Paints, thinners, adhesives
Ethylbenzene	Paints, varnishes, pesticides, adhesives
Xylenes	Paint, varnishes, adhesives
1,2,4-Trimethylbenzene	Gasoline, car exhausts
Naphthalene	Cigarette smoke, insecticides, car exhausts
Styrene	Adhesives, cigarette smoke, car exhausts
Terpenes	
α-Pinene	Fragranced consumer / cleaning products
d-Limonene	Fragranced consumer / cleaning products
Carbonyls	
Formaldehyde	Building materials, furniture, wood products
Acetaldehyde	Building materials, laminate, varnishes, paints
Acetone	Cleaning products, nail polish remover
2-Butanone	Paint, adhesives, cleaning products, car exhausts
Halogenated	
Dichloromethane	Paint strippers, insecticides, hairspray, cleaners
Tetrachloroethylene	Dry-cleaned clothing

Compared to half a century ago, there have been significant changes in the use of consumer products and building materials with impacts on both the concentrations and diversity of VOCs found indoors. In parallel there has been a move towards energy-efficient buildings with improved insulation and reduced air leakage and ventilation [43, 44]. Sick or Tight Building Syndrome is a term that has been used to describe circumstances whereby occupants within a building experience health-related effects or discomfort that seem to be related to the duration spent in a building. In such cases no specific cause can be found and relief from the symptoms, i.e. eye, nose and throat irritation and headaches, is typically experienced upon exiting or moving away from the building [45-48]. These building related symptoms have been reported to have increased discomfort and negative health effects, and result in reduced productivity at work and in schools [45, 49].

Many VOCs compounds can be oxidised to form more harmful secondary products, particularly if they contain reactive carbon double bonds [50-52]. There have been studies associating VOCs to negative health effects in humans; Billionnet et al. found that high concentrations of VOCs were associated with a higher risk of asthma and rhinitis in adults [53]; Arif et al. reported that exposure to VOCs may lead to adverse health consequences [54]; Rumchev et al. reported the association of VOCs with asthma in children [55, 56]; results from the study by Norbäck et al. suggested that indoor VOCs may be related to asthmatic symptoms [57].

Monoterpenes are one class of VOCs found indoors that have high reactivity with hydroxyl (OH) radicals, ozone and nitrate (NO_3) radicals. Many hundreds of different structures are possible in nature and they are released from a very wide range of sources including cooking, foodstuffs, plants and multiple kinds of fragranced products. In practice only a small number of monoterpenes are found in high abundance reflecting the common use of certain individual chemicals

(such as d-limonene and α-pinene) in multiple products. There have been previous measurements of VOCs in homes (see Table 1.3) whereby high concentrations of particularly aromatics and terpenes were reported [39, 58-63].

Table 1.3. Previous measurements of VOCs in homes

Study	Location	VOCs with highest concentrations	Highest concentrations of VOCs (μg m^{-3})	Reference
Chin et al.	Homes in Detroit, Michigan, USA	Aromatics, terpenes (d-limonene and α-pinene), alkanes, tetrachloroethene.	d-Limonene mean = 22.6 α-pinene mean = 4.4 Toluene mean = 11.62	39
Raw et al.	Homes in England	d-Limonene and toluene.	d-Limonene mean = 6.2 Toluene mean = 15.1	58
Jia et al.	Homes in Ann Arbor, Ypsilanti and Dearborn in Michigan, USA	Aromatics, chloroform, alkanes and terpenes.	d-Limonene mean = 25.7 α-pinene mean = 9.0 Toluene mean = 15.6	59
Villanueva et al.	Homes in Puertollano, Spain	Alkanes, terpenes and aromatics.	d-Limonene mean = 17.1 α-pinene mean = 18.5 Toluene mean = 12.0	60
Schlink et al.	Homes in Leipzig, München, and Köln, Germany	Aromatics, terpenes and alkanes.	Terpenes mean , median = 63.5, 36.1 Aromatics mean, median = 56.5, 37.2 Alkanes mean, median = 47.5, 24.0	61
Xu et al.	Homes in Canada	Toluene, d-limonene and α-pinene,	d-Limonene mean = 40.1	62

		with d-limonene and α-pinene predominantly from indoor sources.	α-pinene mean = 11.5 Toluene mean = 15.5	
Langer et al.	Homes in Sweden	Terpenes and toluene.	d-Limonene mean = 15.1 α-pinene median = 5.1 Toluene median = 7.3	63

In terms of chemistry, d-limonene and α-pinene are unsaturated monoterpenes which are susceptible to ozonolysis by the electrophilic attack of ozone on the C=C double bonds, forming an unstable ozonide intermediate which breaks down into two possible combinations of a carbonyl and a Criegee biradical [64, 65]. Intermediate reactive radicals, such as OH, are formed in this reaction [64, 65] which could further react with indoor VOCs and contribute to the further formation of indoor oxidised VOC products [66, 67]. Oxidation products of d-limonene include formaldehyde and 4-acetyl-1-methylcyclohexene, and those of α-pinene include formaldehyde, acetone and pinonaldehyde [68]. Examples of the chemical reactions are shown in Figure 1-2.

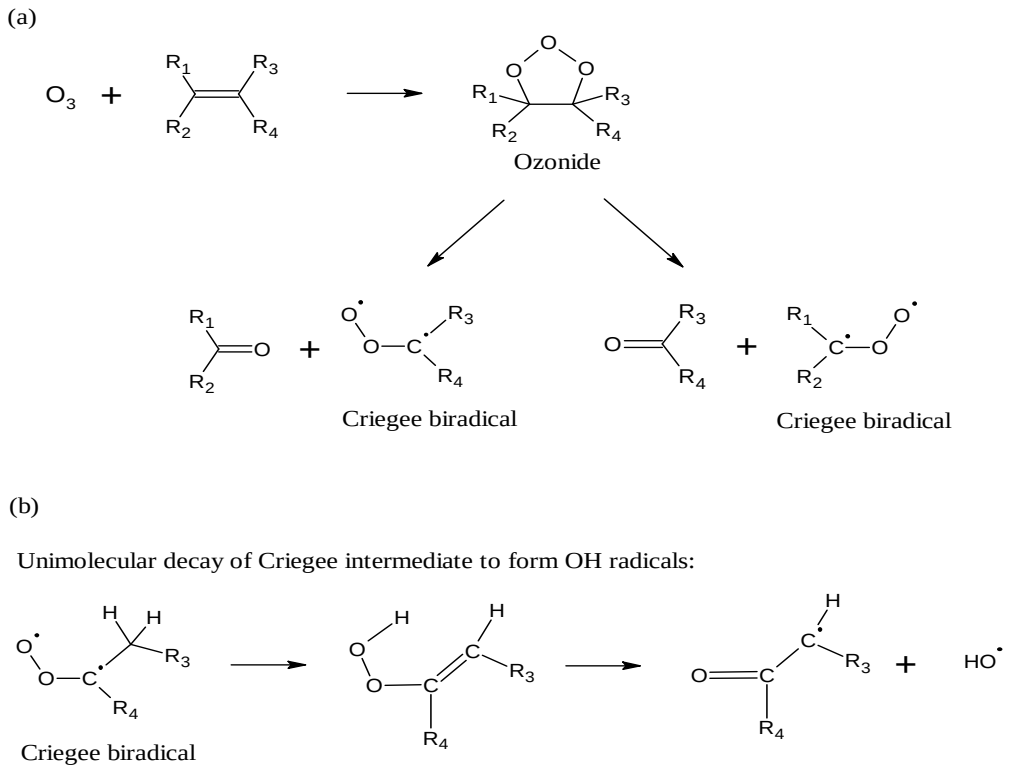


Figure 1-2. (a) Reaction of unsaturated compounds with ozone and (b) formation of OH radicals from Criegee biradicals.

1.2.2 Cyclic volatile methyl siloxanes in the indoor environment

Cyclic volatile methyl siloxanes (cVMS) are manufactured chemicals that are widely used in the production of personal care products and other consumer products such as fragrances, deodorants, lotions, toothpaste, household cleansers and furniture polishes [69-72]. These cVMS include hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5) and dodecacyclohexasiloxane (D_6) (D refers to the dimethylsiloxane unit, and the subscript refers to the number of silicon bonds). As a result of their unique physiochemical properties of being inert and having a smooth texture, low surface tension, high thermal stability and good compatibility with other formulation ingredients, cVMS have become the basic ingredients as emollients or carrier solvents in the manufacture of consumer products. Figure 1-3 shows the structures of D_3, D_4, D_5, D_6.

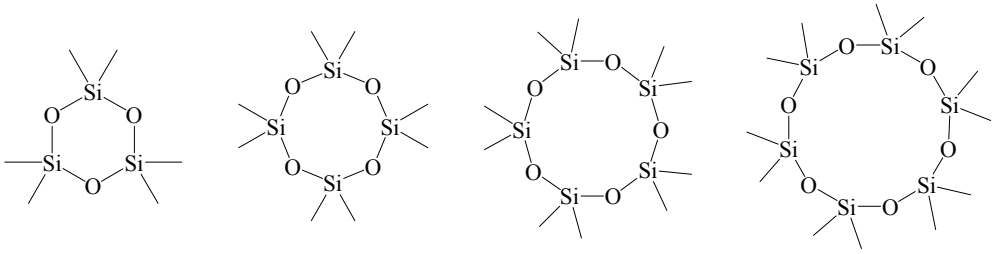


Figure 1-3. Structures of cVMS. From left – right: D_3, D_4, D_5, D_6.

cVMS are of an environmental concern as they are potentially bioaccumulative and persistent with high octanol-water partition coefficient (log K_{ow}) values > 5 and atmospheric oxidation half-life ($AO_{t1/2}$) of more than 2 days [73]. In addition to these characteristics, cVMS are also highly volatile, and therefore have substantial potential for atmospheric long-range transport [74, 75].

There have been measurements of cVMS in the indoor and outdoor environments, with higher concentrations observed indoors [76-81]. Previous studies have also

reported high concentrations of cVMS in cosmetics and personal care products [69, 71]; Wang et al. detected D_4, D_5 and D_6 concentrations as high as 11, 683 and 97.7 mg g^{-1} wet weight respectively in a sample of personal care products, cosmetics and baby products in Canada [69]; Horii et al. reported D_4, D_5, and D_6 concentrations of up to 9.38, 81.8 and 43.1 mg g^{-1} respectively in a sample of cosmetics and personal care products obtained from retail stores in the USA and Japan [71]. The high concentrations from cVMS in these products indicate that they could be an important source of cVMS to the environment. In a recent study by Tang et al., cVMS, in particular D_5, D_4 and D_6, contributed to about a third of the total indoor VOC mass concentration indoor in a classroom, with their source largely associated to emissions from humans [82]. cVMS were found to be the most abundant VOC in a classroom with a distinct association with occupancy [83].

1.3 Measurement of VOCs

There is a range of different types of chemicals that are found in the indoor environment, and hence this necessitates the use of a complex method of analysis, such as gas chromatography - mass spectrometry, for the detection and quantification of the compounds found in indoor air samples.

There are numerous techniques and instruments used for the detection and measurement of VOCs, mostly based around gas chromatography (GC) and mass spectrometry (MS). Some examples are summarised in Table 1.4, together with the respective trade-offs of each method for field analysis. In very general terms, the development of a VOC instrument starts with laboratory standard devices, such as GC and MS, with modifications and additions then made to accommodate a trace level gaseous sample matrix. The key front-end adaptation to all chromatography-based systems is the inclusion of a thermal pre-concentration step, which strips VOCs from litre volumes of air and introduces them to the GC

column with a concentration factor of up to 1000. A consequence is that most instruments in the literature for VOC detection are essentially hybrid lab instruments, not devices intrinsically designed with size, power or weight as constraining factors.

GC is a commonly used technique for the analysis of VOCs and it allows for the detection and quantification of a broad range of compounds that have reasonable volatility and thermal stability. There are two types of columns for GC: packed columns and open tubular columns (also known as capillary columns). Packed columns are generally made of glass or stainless steel, and are filled with the stationary phase or contain a solid support material coated with the liquid stationary phase. They are usually 1.5 – 6 m in length, and have diameters of 2 – 4 mm [84]. Capillary columns, on the other hand, can have lengths as long as 100 m and diameters as small as 0.1 mm, and therefore have higher efficiency (number of theoretical plates and separation power) [84]. There are a few forms of capillary columns: wall-coated open tubular (WCOT) columns, support-coated open tubular (SCOT) columns, and fused-silica wall-coated (FSWC) open tubular columns. In WCOT, the internal capillary wall is directly coated with a thin film of liquid stationary phase, whereas in SCOT the capillary wall is first lined with a thin layer of adsorbent solid, which is then coated with the liquid stationary phase. The FSWC column is a special type of WCOT that is drawn from pure silica and is much thinner than glass WCOT columns. The FSWC column is treated with a polyamide coating to protect it and allow it to be wound into coils. As a result of its flexibility, inertness and greater column efficiency, it is the most popular and commonly used column in analytical GC [84].

Figure 1-4 shows the two different types of GC column [85].

Given the limitations of current technologies for field analysis of VOCs, this work aims to address these issues and develop a portable sensor for the detection and

analysis of VOCs, combining elements of thermal desorption (TD), gas chromatography (GC) and photoionsation detection (PID), but in a device built bottom up, rather than from standard lab equipment.

Figure 1-5 shows a schematic of a typical TD-GC-MS set up used in the laboratory for the analysis of gaseous samples (in silica-treated canisters).

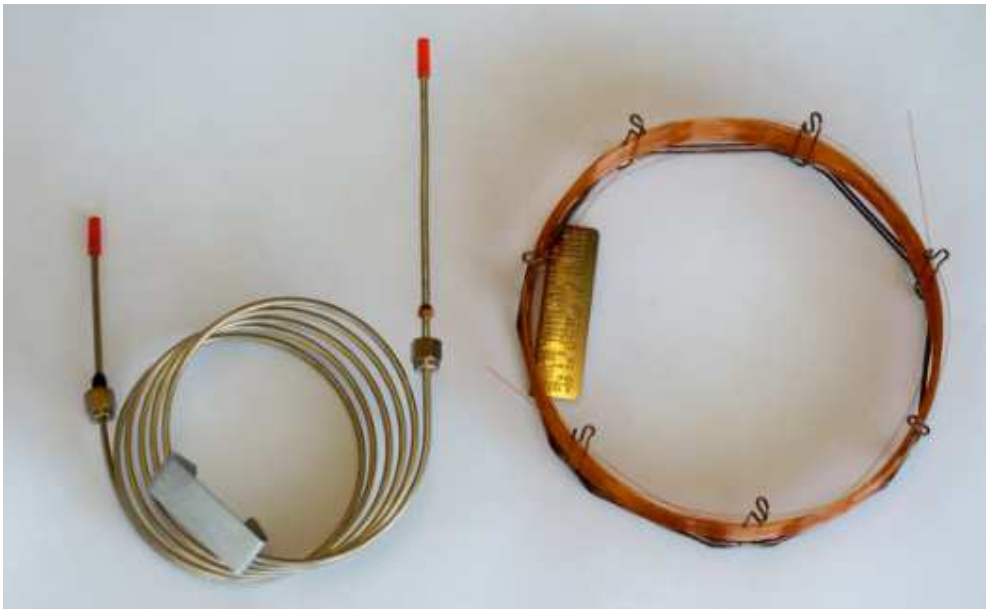


Figure 1-4. Left: Packed GC column; Right: Capillary GC column.

Table 1.4. Current measurement methods for VOCs.

Current measurement methods and its characteristics	Pros	Cons
Thermal desorption - Gas Chromatography with Flame Ionisation Detectors (FID) ▪ Most commonly used in laboratories for VOCs detection.	• Very sensitive and linear in response, and compound calibration can be based in part on a per carbon atom response function. • Good in serviced laboratories or for fixed site observatories. • Stable and reliable when operated autonomously.	• Not selective: The FID will respond to all organic compounds (except HCHO), so identification is based on retention times. Issues due to co-elutions; unable to identify unknown compounds. • Not typically portable due to of its size, mass. Requirement for hydrogen gas is a major constraint on portability.
Bulk Photoionisation Detection (PID) ▪ Utilises an ultraviolet (UV) light source to break down VOCs in the air into positive and negative ions. ▪ Detection of the ions results in a current flow with a magnitude proportional to the concentration of	• Portable detector suitable for field applications because of its small size and no need for supply gases. • The trade-off between using the PID or the FID in detection of VOCs has been discussed [86]; the FID gave well-resolved peaks whereas peak tailing was an issue when the PID was	• Operated in isolation the PID is not selective: will respond to all organic compounds. • Each VOC has a different ionisation potential, which requires calibration.

VOCs present.	used. However, the low-power demands of the PID and its portability were advantages that the FID would not be able to provide.	
Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) ▪ Air is pumped through a drift tube reactor, and a fraction of the VOCs is ionized in PTR with hydronium ions [87]. ▪ Soft ionization method; does not lead to fragmentation of the product ions. ▪ Reagent and product ions are measured by a quadrupole mass spectrometer; signal is proportional to the VOC mixing ratio.	• Allows numerous VOCs of atmospheric interest to be monitored with a high sensitivity (10 – 100 pptv) and rapid response time (1 – 10 sec). • Does not require any sample treatment such as drying or pre-concentration, and is thus well suited for oxygenated VOCs, which cannot be quantified from canister samples. • Provides a fast-response measurement of several key atmospheric VOCs, and complements the highly sensitive and chemically detailed snapshots obtained by GC techniques.	• Only determines the mass of product ions, which is not a unique indicator of the VOC identity. • Isomers cannot be distinguished, and the interpretation of mass spectra is further complicated by the formation of cluster ions and the fragmentation of product ions. • Not easily portable for field measurements. • 200K – 400K USD hardware costs.

Thermal Desorption GC-MS ▪ Sample collection using either packed adsorbent tubes of canisters. ▪ Samples preconcentrated by thermal desorption. ▪ Typically uses quadrupole MS detection, but also increasingly TOF is applied.	• Sensitive and accurate means of retrospective analysis of VOCs adsorbed in soil samples [88, 89], other solids[90, 91], liquids [92, 93] and gases [94-96]. • Sensitive and flexible, compound identifications available from mass spectra. • Capable of identifying unknown compounds in an air sample via MS libraries. • More sensitive from similar FID systems if operated in selected ion modes.	• Size and mass of the bench-top instrumentation render this method unsuitable for field analysis. • More challenging to calibrate and less stable when operated continuously. • Water can be a significant interference. • Higher cost, more complex and typically requires thermostated lab environment for optimal operation. • Several kilowatt power requirement.
Colorimetric (“Stain”) tubes i.e. Draeger tubes ▪ Tube readings in the form of colour changes and intensities.	• Inexpensive method of measuring classes of toxic gases and vapours.	• Tubes have to be continuously observed to ensure that there is no sudden complete discoloration. • Ultra-violet radiation may result in a change in the discoloration [97]. • Readings in the form of colour changes and intensities are subjected to human interpretation.

		• Not VOC specific.
Metal Oxide Semiconductor (MOS) sensors	• Compact and low cost sensors with high sensitivity and short response time.	• Also respond to inorganic gases [98]: problem when trying to measure trace or low concentrations of VOCs in the presence of gases such as NO, NO_2 or CO which are found in the surrounding air. • Not favourable in the field measurement of VOCs because of the lack of selectivity and control of the sensor response.

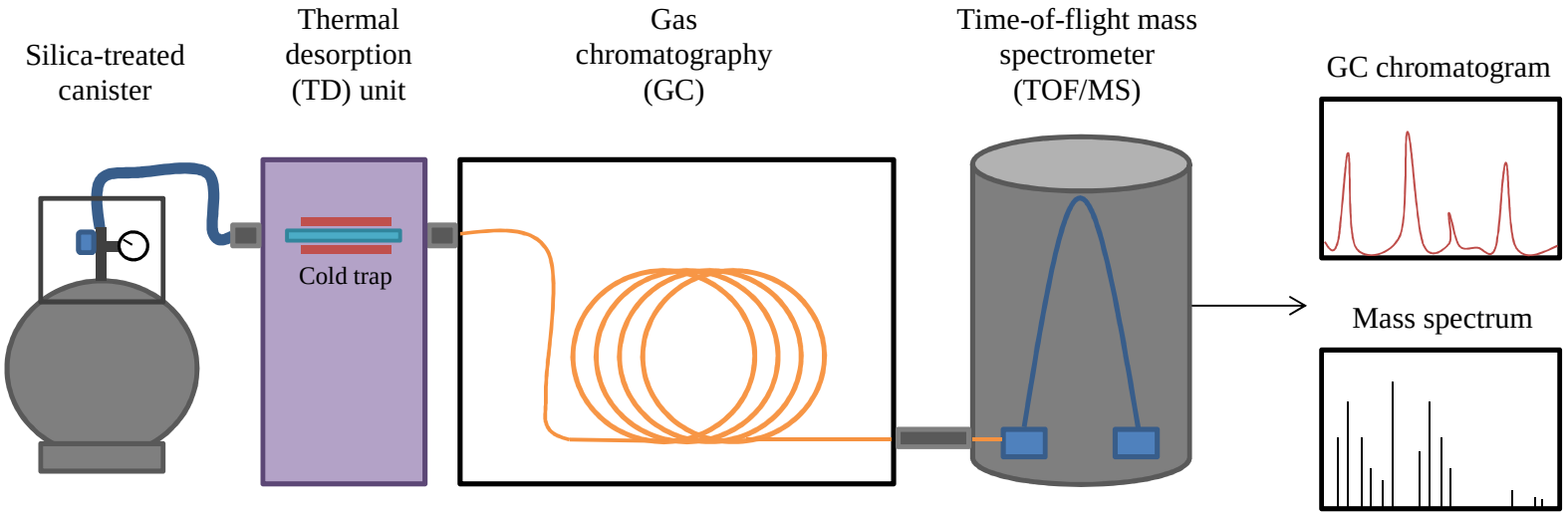


Figure 1-5. Schematic of a typical laboratory set-up for the analysis of gaseous samples.

1.4 Miniaturisation through a lab-on-a-chip device

For the field measurement of VOCs, there is a need for a portable device that provides reliable information on a range of different VOCs, since the impact on downstream effects such as ozone and aerosol formation and health toxicology are structure-specific. Field measurements of VOCs are important in a range of disciplines including air pollution science, medical diagnostics and security screening. There is an enduring need for a portable device that provides reliable compound-specific measurements, at mixing ratios in the part per billion and part per trillion ranges. Bulk measurements (e.g. total carbon mass per unit volume) of VOCs do not provide sufficient detail on the precise VOC composition to be useful in most environmental and health applications. Any portable device should be robust, low-cost and have low-power demands, since many applications are likely to be off-grid. The development of a lab-on-a-chip (LOC) device requires a collaboration of multiple disciplines, involving research and development from different fields in sciences and engineering. This is necessary for the assembling and integration of sample collection and preparation stages, gas chromatography (GC) separation stage and photoionization detection (PID), to create a complete functional system.

The literature on GC-LOC dates back to 1970s: Terry et al. described the development of a miniaturised GC system whereby capillary channels and valves were fabricated on a silicon wafer by photolithography and chemical etching techniques, and a nickel resistor thermal conductivity detector was used as the detection method [99]. The idea of miniaturization and LOC was a result of the growing environmental demands for reduced consumption of sample and reagent solutions. There was a move towards the development of multi-analyte analysers that could be used for environmental monitoring purposes. The first generation of flow injection (FI) led to the development of the second generation sequential

injection (SI) analysis in 1990 [100] which was later followed by the creation of lab-on-a-valve (LOV) in 2000 [101]. The LOV was seen as a downscaled analytical tool and fluidic universal system for reagent-based assays at the low microliter level, which was versatile and had the potential to incorporate different sample preparation procedures in its process. Figure 1-6 [100] and Figure 1-7 [101] show the schematics of a SI analyser and a LOV respectively.

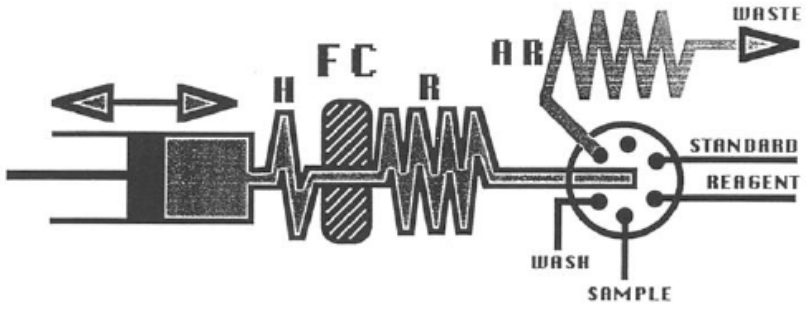


Figure 1-6. Configuration of a sequential injection analyser where H = hold-up conduit, FC = flow cell, R = reactor coil and AR = auxiliary reactor [100].

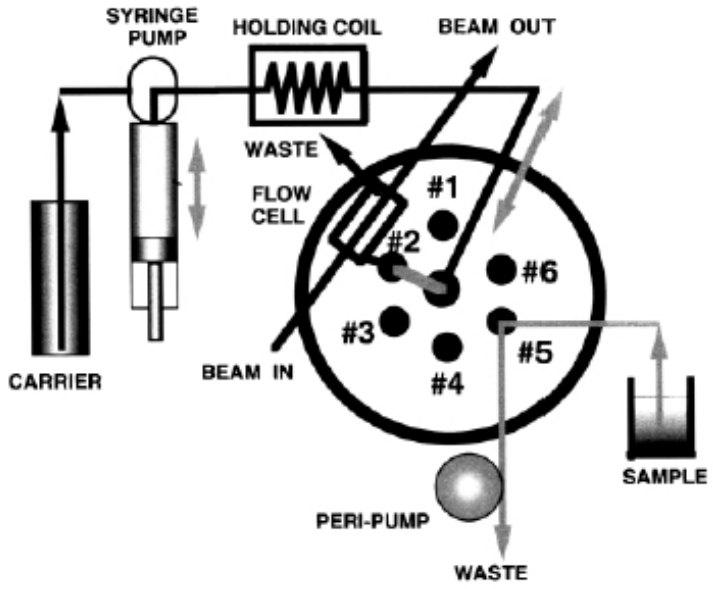


Figure 1-7. Micro sequential injection system (LOV) with the central sample processing unit integrated with a flow cell for optical detection mounted atop a six-position valve [101].

In the recent years, much intensive research has been conducted with regards to the miniaturizing of flow systems, resulting in the development of LOC (or micro total analysis systems, μTAS). The fabrication of such systems is to allow the automation of standard laboratory practices in a miniaturized format, with the obvious advantages of lower consumption of sample and reagents, possibility of separations with higher resolutions, low cost set-ups and shorter analysis duration [102]. Another advantage pointed out in the same review paper by A Rios et al. is that the automation of laboratory processes on a chip would reduce the need for highly skilled personnel to handle complex equipment [102]. Much of the research work on LOC has been predominantly carried out by electrical and mechanical engineers in research institutions. The channel network, which is made by various sophisticated procedures, such as micro-drilling, etching, photolithography, or laser erasing, is impressively exact and reproducible, allowing different channels

profiles to be obtained. As mentioned by Miro and Hansen, these LOCs "can be made in inexpensive materials, namely silicon, glass, polymethyl methacrylate and polydimethylsiloxane, and mass-produced at low cost, in fact, at much lower expenditures than the LOV. However, the microfluidic devices are usually dedicated, that is, they have fixed architecture for predetermined chemistries." [103]

There is yet another interesting emerging technology that harbours similar aims and advantages brought about by LOC – to be affordable and robust, yet sensitive and specific for its usage. This emerging development is known as microfluidic paper-based analytical devices (µPADs) which comprises of microfluidic channels on paper instead of glass or plastic as in LOC devices. Movement of fluids within the channels in µPADs is via capillary action, hence eliminating the need for pumps or valving mechanisms to control fluid flow. Detection means for these devices are usually electrochemical or colorimetric [104-107]. Figure 1-8 [107] shows the schematic of a paper-based electrochemical sensing microfluidic device.

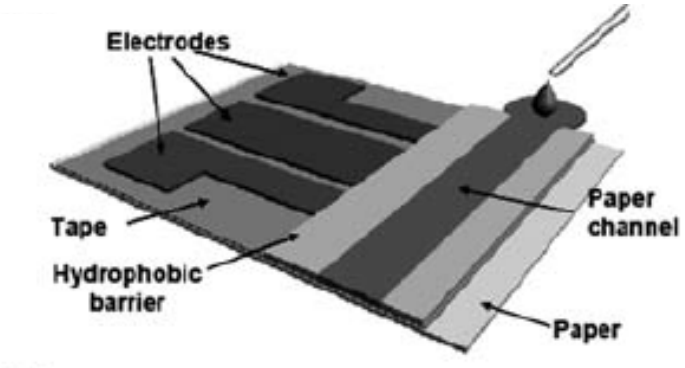


Figure 1-8. Schematic of a paper-based electrochemical device, comprising of a paper channel in conformal contact with the electrodes printed on a piece of paper.

As a result of the portability of LOCs, its potential to be used for in-field real-time monitoring of the environment has been realised [108]. There was the flexibility of obtaining almost-immediate analytical results at high temporal and spatial

resolution, and at low cost without the need to bring the samples back to the chemical laboratory for off-site analysis. Despite the obvious advantages brought about by LOCs, there are still doubts and criticisms on the real applicability of LOCs for real sample analysis. It has been said that "there is often no limitation as regards to the available volume of environmental sample as opposed to assays in the forensic, clinical and bioanalytical areas" [109], indicating that LOCs may be redundant in the environment field. In the same review by Miro and Hansen, it was pointed out that the use of LOC with sample volumes of as low as nano-litre level may result in an issue with the representativeness of the sample obtained. It brings into question the reliability of the results when LOC is used as a mean of obtaining a measurement [109]. In addition, LOC devices may not be developed enough at this moment to cope with complex sample matrices, such as soil, which still requires sample preparation and clean-up procedures before they can be introduced to the LOC for detection. This is perhaps the biggest limitation faced by LOC devices in the environment field as they have to deal with the clogging of channels as a result of the introduction of particles that are present in the sample matrices.

1.4.1 LOC for gas phase analysis

Much of the problems and concerns associated with LOC are to do with the sample preparation of complex matrices, such as aqueous and soil samples from the environment that require clean-up steps prior to the detection of the desired analytes in these samples. There have been, however, reports of promising developments in the field of gas phase sensors involved in sample preparation procedures prior to detection and analysis of the analytes. A microfluidic lab-on-chip derivatisation technique has been optimized to achieve a rapid, automated and sensitive determination of ambient gaseous formaldehyde when used in combination with GC-MS. The method used a Pyrex micro-reactor comprising

three inlets and one outlet, gas and fluid splitting and combining channels, mixing junctions, and a reaction micro-channel. The micro-reactor integrated three functions, that of: mixer and reactor, heater, and preconcentrator. The flow rates of the gas sample and derivatisation solution and the temperature of the micro-reactor were optimized to achieve a near real-time measurement with a rapid and high efficiency derivatisation step following gas sampling. The enhanced phase contact area-to-volume ratio and the high heat transfer rate in the micro-reactor resulted in a fast and high efficiency derivatisation reaction [19]. This concept has also proven to be successful for the derivatisation of other carbonyls, with method detection limits (MDLs) below or close to their typical concentrations in clean ambient air [110]. Microfluidic derivatisation is attractive for many reasons; of relevance here for field measurements are its economical consumption of reagents and energy. An advantage of undertaking reactions in microfluidic systems is that enhanced reaction efficiency may be achieved due to a high phase contact area-to-volume ratio in micro-channels.

Figure 1-9 shows the layout of the micro-reactor used for the derivatisation of the carbonyls [110].

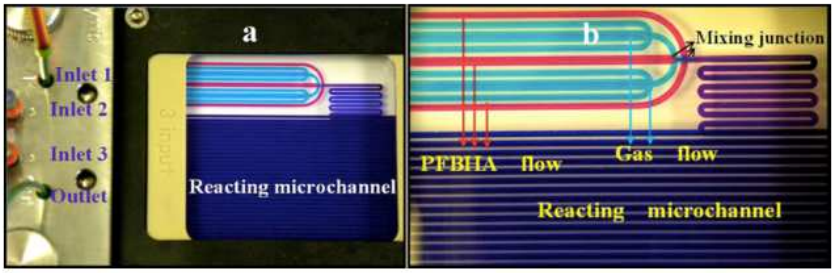


Figure 1-9. Micro-reactor for the derivatisation of carbonyls.

One important factor for good GC separations is the uniform heating of a GC column. The heating of GC columns by conventional means is primarily based on the turbulent fan oven, which is an excellent means to achieve even heating of the column. However the size of such ovens renders this a difficult technique to use in

remote locations for field analysis in environmental research. The single planar fabrication of the micro-reactor mentioned above incorporates all subcomponents of the GC system in a structural geometry that is much easier to heat using planar devices. Uniform heating is central to the performance of GC, requiring accurate and reproducible column temperatures and with minimal spatial temperature gradients. Direct resistive heating and cooling of the glass chip involving a stack of thin film resistive elements and Peltier devices produced a uniform heating profile across the column when held at both above and below ambient temperatures. The low thermal conductivity of glass allowed for multiple temperature zones within the same chip. The power required to achieve column temperatures ranges from 10 – 200ºC was about 25W, two orders of magnitude less than conventional turbulent fans ovens. A figure of what has been done with respect to heating and cooling of the chip is shown in Figure 1-10 [111].

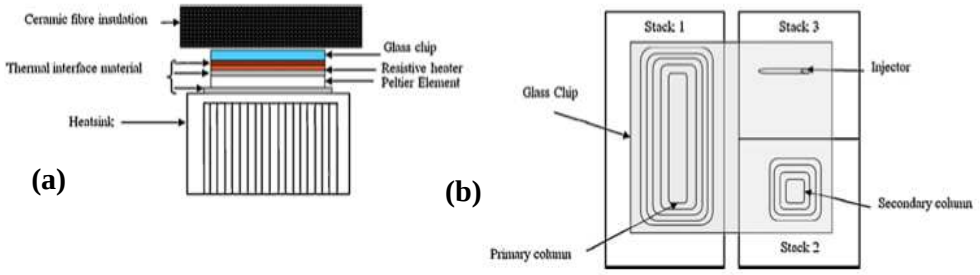


Figure 1-10. (a) Layout of components in the temperature controlled stack used for heating and cooling of the glass GC. (b) Plan view layout of the temperature controlled stack.

It has also been proven that the microfabricated gas chromatography system is suitable for the separation of volatile organic compounds (VOCs) and compatible with use as a portable measurement device with the PID [112]. A standard FID and a modified lightweight 100 mW photoionization detector (PID) were coupled to the column and performance tested with gas mixtures of monoaromatic and

monoterpene species at the parts per million concentration level. The low power GC-PID device showed good performance for a small set of VOCs and sub nano-gram detection sensitivity to monoaromatics.

1.5 Summary of project

The objective of this project is to understand the major compounds found in indoor environments and to develop novel ways to measure them. Studies on indoor air sampling and analysis will be carried out to better understand the current distribution of VOCs in their concentrations and speciation in indoor environments. Research on novel methods of sampling and analysis suitable for cVMS will also be carried out – such methods should allow for indoor sampling to be conveniently conducted.

This work will also include the development of a multispecies sensor for measuring hydrocarbons and oxygenated compounds in gas phase samples, through the deployment of thermal desorption methods in combination with a micro-fabricated GC-PID device. The final developed system will allow measurements of a range of different organic compounds found in indoor air. This will be validated using controlled experiments and against reference standards and measurement techniques. The system will be applied in number of real-world monitoring investigations, including indoor atmospheres and air pollution studies.

This thesis will first describe in Chapters 2 and 3 the studies on indoor air sampling and analysis that were conducted. Chapter 4 will describe the work that was done with regard to the sampling and analysis of cVMS, a class of compounds that were detected in the indoor air studies. Finally, Chapters 5 and 6 will describe the development of a portable sensor that would be suitable for the detection and measurement of VOCs in the indoor environment.

Chapter 2

Indoor air analysis: Unexpectedly high concentrations of monoterpenes in a study of UK homes

2.1 Introduction

This chapter provides an estimate of current concentrations, speciation and variability of VOCs in UK homes in 2015, providing an updated set of estimates of the predominant indoor air composition at this time. The study used whole air sampling, the default method for high precision sampling outdoors and applied this indoors alongside a universal GC-TOF/MS analysis. By using whole air samples and GC-TOF, rather than adsorption tubes (which are the more commonly used indoor method) skewing of sampling based on compound volatility is largely eliminated and this allows a quantification of volatiles such as isoprene.

The data reported in this work combined two different studies conducted in London and York in 2015. In total 25 homes were sampled on multiple occasions, 19 in London representing homes of diverse property types, ages and occupant density. The remaining 6 homes were located in York and were of very similar age (~2000) and building design. The samples collected from the 19 London homes were used to improve understanding of the current distribution across a property mix in a major city, and the repeated sampling of 6 similar modern-build homes in York to understand how current variability in VOCs concentrations and speciation can be driven by occupant behaviour.

The concentrations of VOCs in the 25 UK homes were quantified using continuous indoor air sampling over five days. Air was collected through low flow (1 mL min^{-1}) constant flow restrictors into evacuated 6 L internally silica-treated canisters until the canister reached atmospheric pressure. This was followed by thermal desorption-gas chromatography and high mass accuracy time-of-flight mass spectrometry (TD-GC-TOF/MS). A fully quantitative analysis was performed on the eight most abundant hydrocarbon-based VOCs found.

2.2 Experimental

Sampling in London and York was carried out in homes which were located in residential urban areas. In both cities information on the air exchange rate of the homes was not collected; there was no available information about the heating, ventilation and air-conditioning (HVAC) systems in the homes, nor the occupants' frequency and duration of opening windows. Whilst details were not collected domestic air conditioning systems are exceptionally rare in UK homes. Figure 2-1 shows the work flow for the indoor air study conducted in London and York.

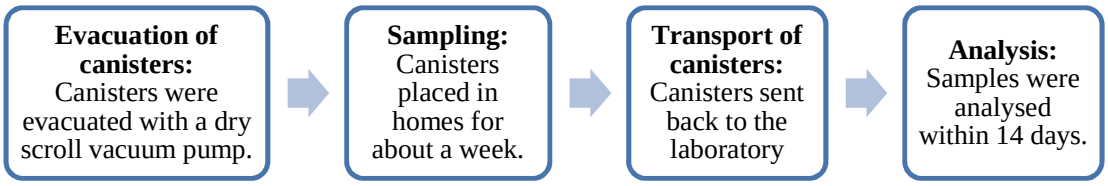


Figure 2-1. Work flow for sampling and analysis of samples from homes.

2.2.1 VOC sampling and analysis

The most common method reported in literature for VOCs sampling indoors is to either passively sample (*via* diffusion) or pump sample air onto chemical adsorption tubes, often packed with Tenax polymer, and various standard methods exist [113-117]. For outdoor air sampling such methods are only infrequently used since the sampling is skewed to the collection of VOCs that have moderate to low volatility whilst more volatile species, for example ethane, propane, butane, pentane and isoprene, pass through the adsorbent bed with poor adsorption [118-120]. Instead we apply the preferred World Meteorological Organisation (WMO) method for measurement of ambient VOCs based on sampling air into initially evacuated whole air canisters. Such an approach collects all VOCs that are present without discrimination and the method allows for multiple repeat analysis of the same sample. The method does not require electricity, uses no chemicals and is

intrinsically safe and suitable for untrained users. A further advantage of stainless canisters is that the effects of ozone on the sample are much reduced, with co-sampled ozone destroyed on contact with stainless steel inlet and walls through autoxidation. No chemical scrubbers are needed [121, 122].

The storage stability of VOCs in canisters has been previously assessed. In a study by Herrington [123], majority of the 66 VOCs evaluated had a recovery of about 100 % after 30 days under dry (0 % RH) and humid (93 % RH) conditions; only acrolein, dibromochloromethane, and bromoform exhibited instability under humid conditions. Good stability of VOCs were also reported for other studies by Lidster et al. [124], Hsieh et al. [125] and Ochiai et al. [126] with no notable loss observed.

To collect the samples in both London and York 6-liter internal volume canisters (SilcoCan, Thames Restek U.K. Ltd) were used followed by analysis using gas chromatography and time-of-flight mass spectrometry (GC-Q-TOF/MS). Using this approach there was no discrimination in the sampling towards VOCs of intermediate volatility. Since we are working only with preserved gaseous samples we then extend this to the calibration using picomole per mole gas standards and with no reliance on the liquid spiking of test materials onto adsorption tubes.

Prior to sampling, the canisters were evacuated with a dry scroll vacuum pump to around 3 x 10^{-3} atm, following the WMO methodology. Each of the canisters was fixed with a constant flow inlet system (Thames Restek U.K. Ltd). This is a critical orifice made from machined 316 stainless steel that allows a constant gas flow through the orifice into the canister, irrespective of the internal vacuum of the canister until the canister reaches ambient atmospheric pressure. This is possible with the flow controller which has a metal diaphragm that regulates the flow as the pressure in the canister changes. The critical orifice inlets allowed a flow rate of ~1 mL min^{-1} until the canister pressure reached ambient pressure after

approximately 5 days. Using this method a true 5-day average concentration is determined.

Prior to chemical analysis the canisters containing sample air at ambient pressure were pressurised from atmospheric pressure to 3 atmospheres with helium (BOC Gases, 6.0 ultra- high purity grade), resulting in a dilution factor later corrected for during quantification. The large sample of gas in each canister allowed for repeated analyses if required, an advantage over sorption tubes. All canisters were analysed within two weeks after completion of sampling to minimise any losses due to physical adsorption, reactions with reactive compounds and degradation [127]. This time period was largely a result of the time needed to effect the collection of samples from participants' homes and the shipping of those samples to York. Blanks were run with canisters containing pressurised helium.

A difference between the method used here and the more traditional methods used for VOCs measurement using adsorption tubes is the use of direct gas phase standards rather than liquids surrogates spiked onto tubes. We use multi-component high pressure VOCs gas standards at the part per billion mixing ratio with a balance gas of N_2 from the UK National Physical Laboratory (NPL). These standards contain ozone precursor hydrocarbons VOCs typically at 4 ppb with a gravimetric preparation uncertainty of 5%. A range of monoterpenes in a gas phase standard from NPL were also available for calibration, the choice of these species taken from the current target list of the WMO Global Atmospheric Watch. The analytical method included a routine calibration of the whole system response to VOCs, achieved through flowing gas calibrant mixtures through the water removal, thermal desorption and the GC-MS procedure. VOCs gas standards and zero samples using high purity helium bracketed the analysis of individual sample canisters.

2.2.2 Thermal desorption

The pressurised air sample was introduced into a thermal desorption unit (Markes Unity Series 2 Thermal Desorption Unit) prior to separation on a gas chromatography (GC) column. A metered flow of sample gas was first passed through a glass cold-finger assembly maintained at a temperature of about -35 ˚C. This served to remove moisture from the gas before it entered the thermal desorption unit, to prevent icing in the adsorbent trap and to reduce the amount of water ultimately entering the mass spectrometer. 1000 mL of gas was sampled at 100 mL min^{-1} onto a refocusing adsorption trap packed with Tenax sorbent. The choice of Tenax as the adsorbent was to specifically support the sampling of monoterpenes, since this material provides the most stable matrix for avoiding molecular rearrangements. The relatively low temperature of the Tenax trap was necessary to allow for the quantitative collection of volatile VOCs, for example isoprene, that were in the sample gas. Once the VOCs were focused on the Tenax trap, it was then was purged for 1 minute at 100 mL min^{-1} with helium to remove permanent gases. After this, the trap was ballistically heated from -30 °C to 300 °C at the maximum heating rate of the system and held for 3 minutes, with the VOCs transferred to GC column in splitless mode at a flow rate of around 1.5 mL min^{-1}. Figure 2-2 shows a schematic of the thermal desorption process.

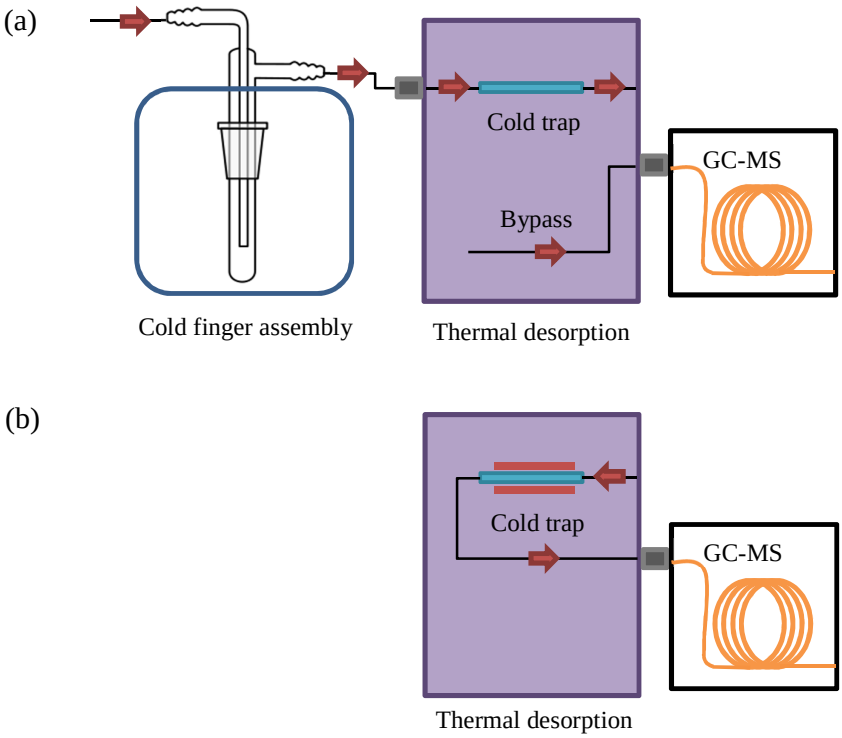


Figure 2-2. Schematics depicting (a) the flow path of gas during sampling and (b) focusing trap desorption.

2.2.3 Gas chromatography and time-of-flight mass spectrometry

High purity helium (BIP Air Products, Keumiee, Belgium) was used as the carrier gas for GC. Separation was performed on a BPX5 column (50 m x 0.32 mm x 1.0 µm, length x internal diameter x film thickness) with two split outlets, one going to the Agilent time-of-flight/mass spectrometer (TOF/MS) and the other going directly into an olfactory port, used either for human assessment or as a mounting for a secondary photoionisation detector (PID). The GC column was programmed to run at 40 ˚C for 3 minutes, then ramp at 15 ˚C min^{-1} to 125 ˚C, then at 20 ˚C min^{-1} to 250 ˚C and held for 2 minutes.

In mass spectrometry, compounds are ionised and separated based on their mass to charge (m/z) ratios. The more commonly encountered mass spectrometer would be the quadrupole mass spectrometer. Figure 2-3 [128] shows a diagram of a quadrupole mass analyser. It consists of four electrically connected metal rods. A direct and alternating voltage is applied between the rods which affects the movement of the ions, and ensures that only ions with specific m/z ratio can reach the detector. The mass and charge of the ion and the strength of the field and frequency of the oscillation determine if the ion will travel down the quadrupole between the rods to reach the detector. Ions with an unstable trajectory will collide with the rods. Simultaneously varying the amplitude of the direct and alternating voltages allows for the detection of ions from small to large m/z values, producing a full scan of a mass spectrum.

The quadrupole mass spectrometer can be used for qualitative and quantitative analyses, and can perform with increased sensitivity in the selected ion monitoring (SIM) mode. Its drawback is its acquisition rate due to its scanning nature, and may lead to spectral bias. A longer scan time is also required for the acquisition of broader mass range spectra.

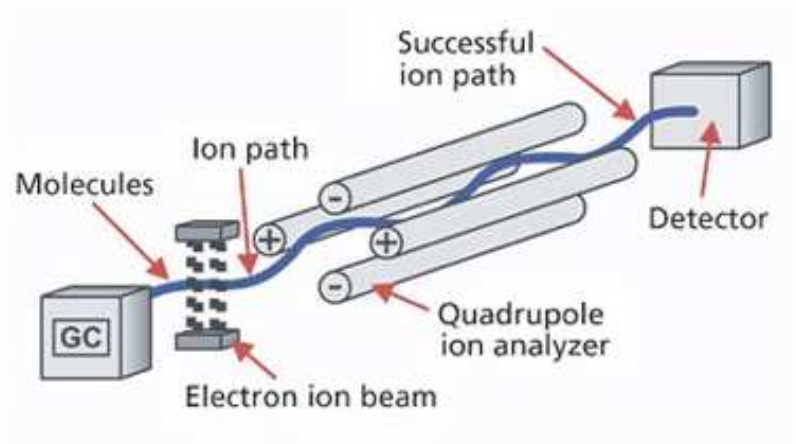


Figure 2-3. Diagram of a quadrupole mass analyser.

The mass spectrometer used in this work is the time-of-flight mass spectrometer (TOF/MS). Ions are separated by time, without the use of an electric or magnetic field. Figure 2-4 [128] shows a diagram of a TOF/MS system.

The potential energy of an ion in an electric field is zU, where z is the charge of the ion and U is the electric potential difference. Ions are accelerated into a field-free region and their potential energy is converted to kinetic energy. Therefore, ions with the same charge are accelerated with the same kinetic energy, $zU = ½ mv^2$, where m is the mass and v is the velocity of the ion. The velocities of the ions depend on their masses – the heavier the ions, the lower their velocities. From the time of flight, t, measured for the ions to reach the detector at a known distance, d, (length of path in the TOF tube/chamber), the m/z ratio of the ions can be calculated:

$$v = d/t$$

$$zU = ½ m(d/t)^2$$

$$t = d/\sqrt{(2U)} * \sqrt{(m/z)}$$

$$\Rightarrow \quad t = k * \sqrt{(m/z)}$$

$$m/z = (t/k)^2$$

A reflectron is added to the TOF mass analyser for the extension of focal length. This is especially crucial for ions with higher masses which may have reduced resolution as a result of the longer flight time and difficulty in reaching the ideal velocities. Ions with the same mass enter the reflector at different times; the ones travelling faster enter sooner than the slower ones. The faster ions will enter deeper into the reflectron before they are reflected, while the slower ones enter later but will not go as deep before they are reflected. As a result, the ions of the

same masses will converge and narrow their range of flight times and the bandwidth of their output signal [129].

In contrast to the quadrupole mass spectrometer, the TOF/MS is a non-scanning instrument, hence having the advantages of faster acquisition rates, spectral continuity and high dynamic range [128]. The acquisition of full mass range spectra can also be obtained without compromising on speed and sensitivity of the analyses. Quantitative analyses with the quadrupole mass spectrometer is usually conducted in the SIM mode; thus for non-targeted compounds, samples would be analysed first for the identification of the compounds, and then again in SIM mode for their quantification. This would however be unnecessary for the TOF/MS. It produces repeatable quantitative results and full range mass spectra for qualitative analyses in one run, making it extremely effective for the analysis of non-targeted compounds.

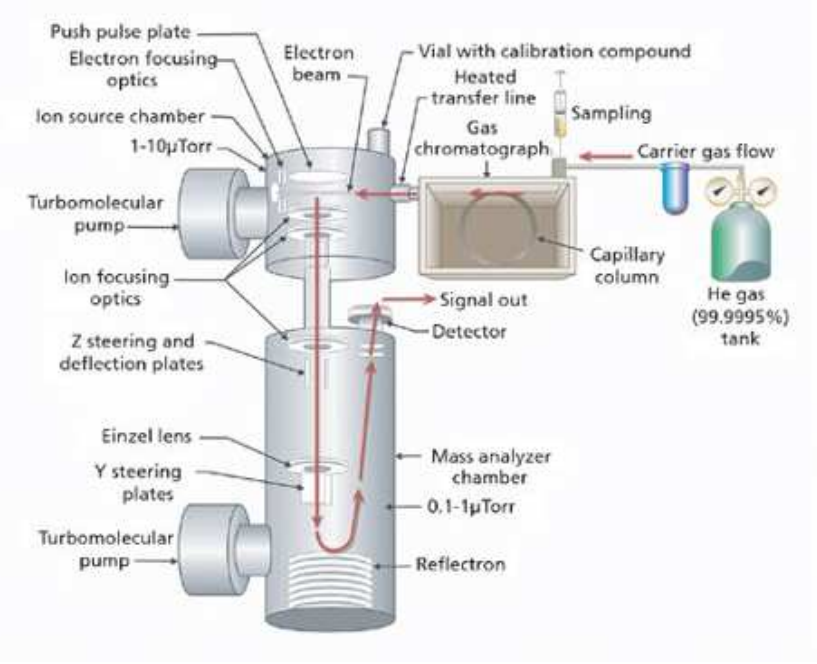


Figure 2-4. Diagram of a TOF mass analyser.

The TOF/MS collected all masses between 45 and 500 amu simultaneously, with data binning to an accuracy of 1 part per million. For subsequent data analysis a mass accuracy of 10 ppm was typically used, providing a good balance between exact molecular elemental composition and sensitivity. The sensitivity of the method is largely defined by the sample volume pre-concentrated on the thermal desorption, any blank or artefact value and the sensitivity of the mass spectrometer to each VOC. The last of these factors varies considerably depending on the fragmentation patterns of the VOCs. For hydrocarbon-based VOCs the blank values are typically not significant in an indoor context and a Limit of Detection (LOD) of around 2 ppt is typically achieved, using 3 x standard deviation definition. A Limit of Quantification (LOQ) is typically 10 ppt for hydrocarbon based VOCs in this system (10 x Std Dev definition), but this is largely irrelevant given the most abundant VOCs are in the part per billion range. For species such as cyclic volatile methyl siloxanes (cVMS), their detection limit is below 1 part per trillion because the fragmentation pattern are highly advantageous and unique. However the LOQ is then very significantly affected by blank and background values and that prevents a quantitative analysis here, even though many cVMS are present in the part per billion range.

An expanded uncertainty in measurement for hydrocarbon-based VOCs can be derived based from the canister to canister sampling reproducibility, canister stability, and analytical run to run reproducibility, combined with uncertainty introduced by the gaseous gravimetric standards. Canister stability is the hardest value to assess since it is potentially unique to each environment tested. Storage of samples in the canisters used here show no statistically significant (that is outside of the measurement uncertainty) changes over periods of two weeks. The expanded uncertainty when the measurand is in the 1-1000 part per billion mixing ratio range is typically 10%, with the gravimetric standards introducing the largest single source of error.

2.2.4 Formaldehyde analysis with HPLC and UV detection

The analysis of formaldehyde was carried out on a high performance liquid chromatography (HPLC) apparatus with elution gradient and ultra-violet (UV) detection. Separation was performed on a reverse phase C_{18} HPLC column (150 mm length, 4.6 mm diameter, 5 µm packing particle size). The detector was set to a wavelength of 365 nm. Flow rate was set at 1.9 ml min^{-1}, and isocratic elution was carried out with acetonitrile/water 38:62 v/v in 10 minutes, and reverse gradient to acetonitrile/water 38:62 v/v in 5 minutes.

The list of the most abundant (as a mass concentration) detectable VOCs compounds in the study is shown in Table 2.1 and it is the eight most abundant hydrocarbon-based species that are then subject to a fully quantitative analysis in this chapter. Figure 2-5 shows the extracted ion chromatograms of selected VOCs at the exact masses of their most abundant ion to confirm their identities using the high mass accuracy of the Agilent GC-QTOF mass spectrometer. The actual mass spectra of isoprene, toluene, *o*-xylene, α-pinene, d-limonene, tetrachloroethylene and decamethylcyclopentasiloxane (D_5) are compared with that of the library as shown in Figure 2-6 to Figure 2-12 (actual mass spectra obtained from the analysis of Home 03 in London). The total ion GC-MS chromatograms and PID chromatograms (see Chapter 5.3 for PID set-up) obtained from the analyses of the homes in London with major peaks identified and other mass spectra are shown in Appendix A. Table 2.2 lists the compounds and the exact masses of their base peaks (or their unique ions) for the identification of the compounds.

Table 2.1. The detected compounds.

VOCs quantitatively analysed	VOCs detected qualitatively
Isoprene	Hexamethylcyclotrisiloxane
Benzene	Octamethylcyclotetrasiloxane
Toluene	Decamethylcyclopentasiloxane
Ethylbenzene	Dodecamethylcyclohexasiloxane
m+ *p*-xylenes	Butan-2-one
o-xylene	1,2-Dichloroethane
α-pinene	Tetrachloroethylene
d-Limonene	Dichloromethane
	Allylmethylsulfide
	Diallylsulfide
	Naphthalene
	3-carene
	p-cymene
	Trimethylbenzenes

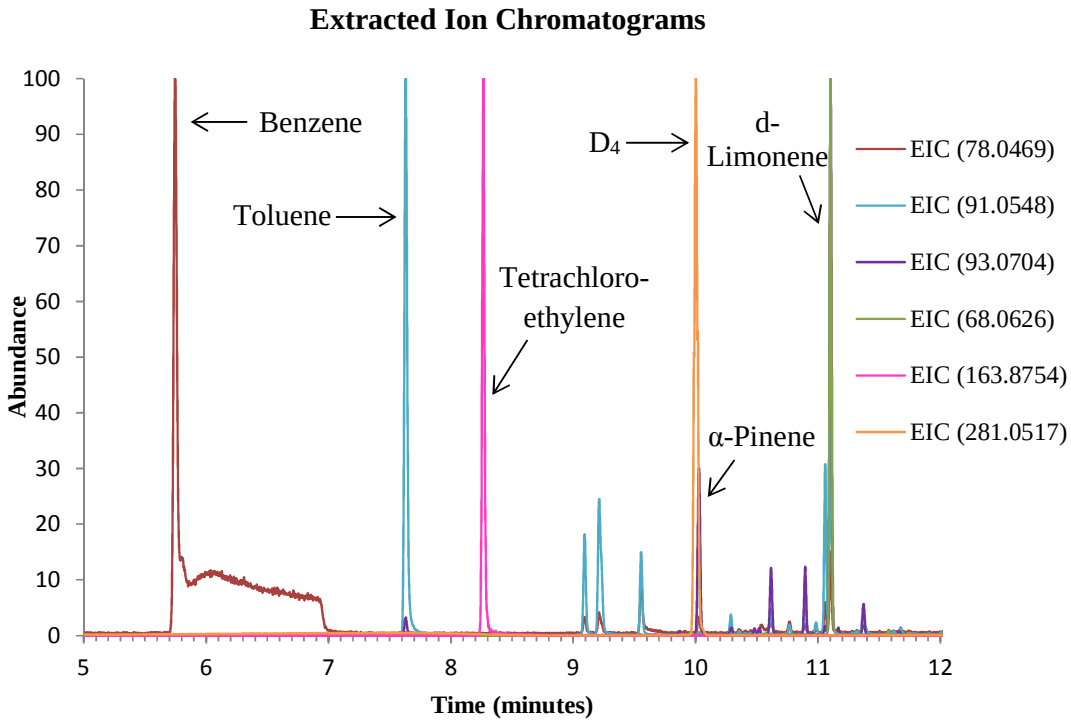


Figure 2-5. Extracted ion chromatographs of selected VOCs at the exact masses of their most abundant ion for one of the homes in London.

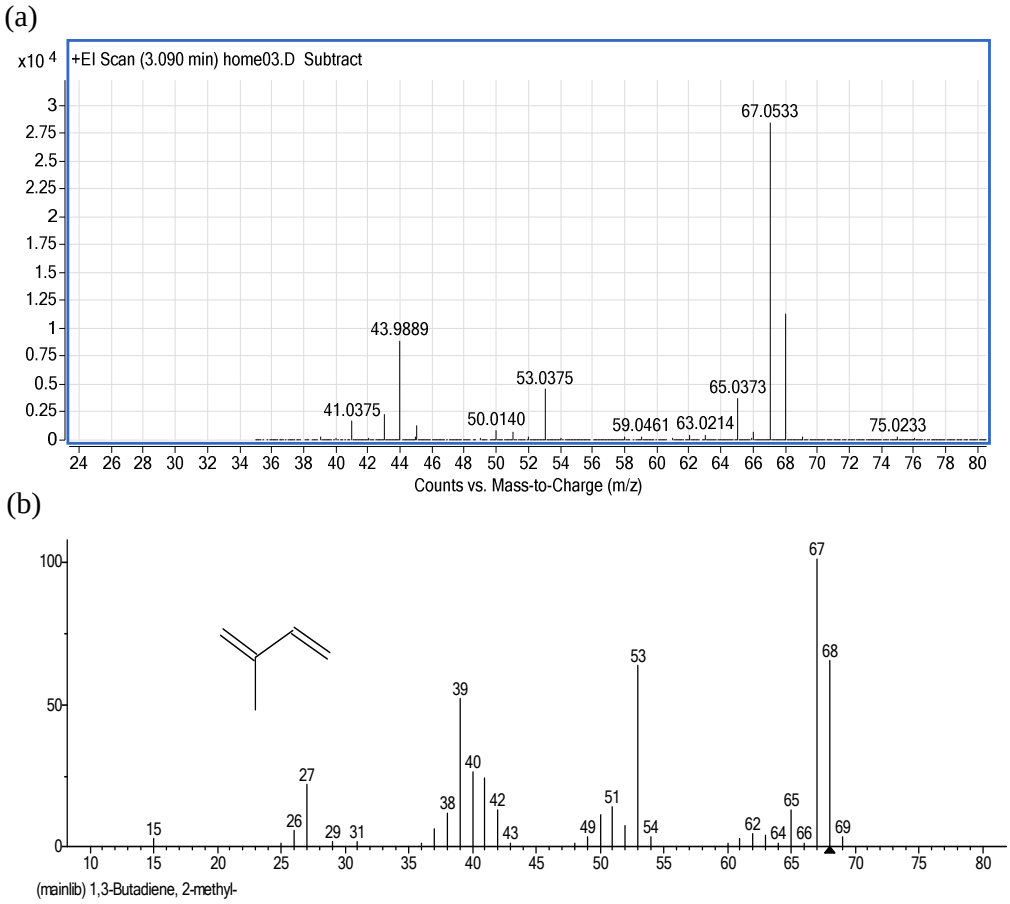


Figure 2-6. Mass spectra of isoprene (a) from Home 03 and (b) from NIST MS library.

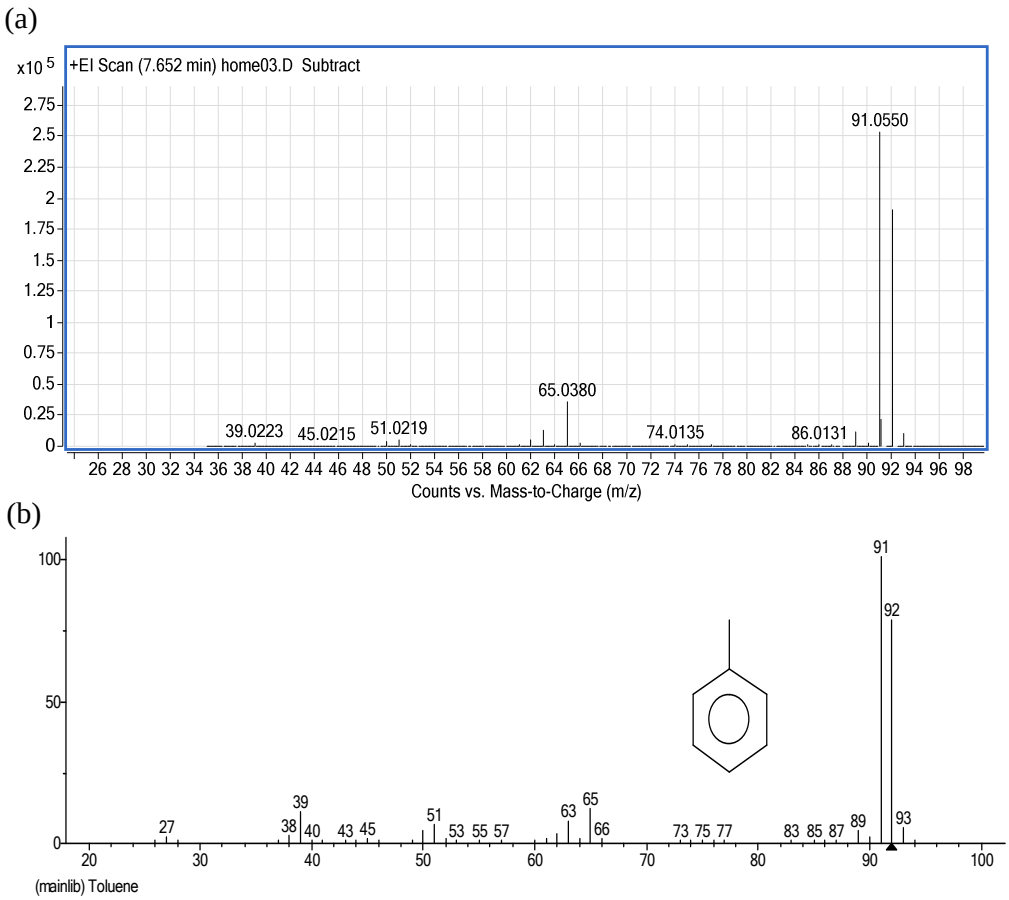


Figure 2-7. Mass spectra of toluene (a) from Home 03 and (b) from NIST MS library.

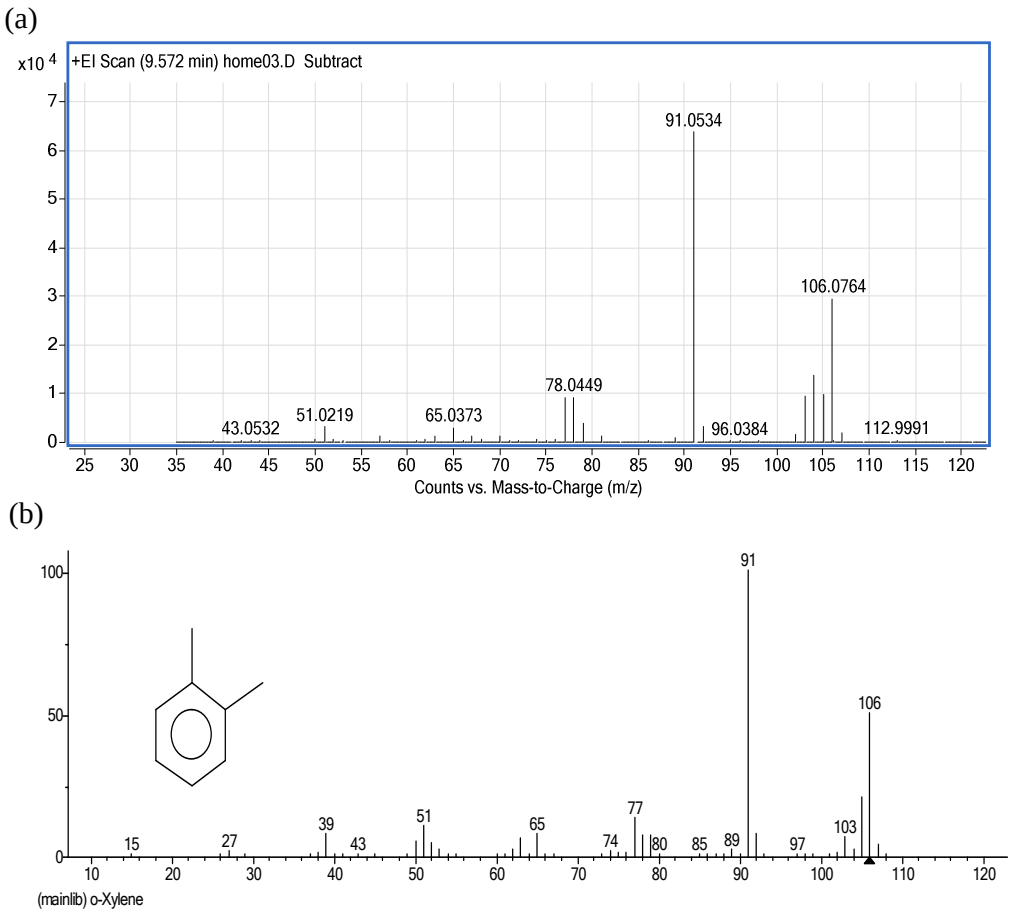
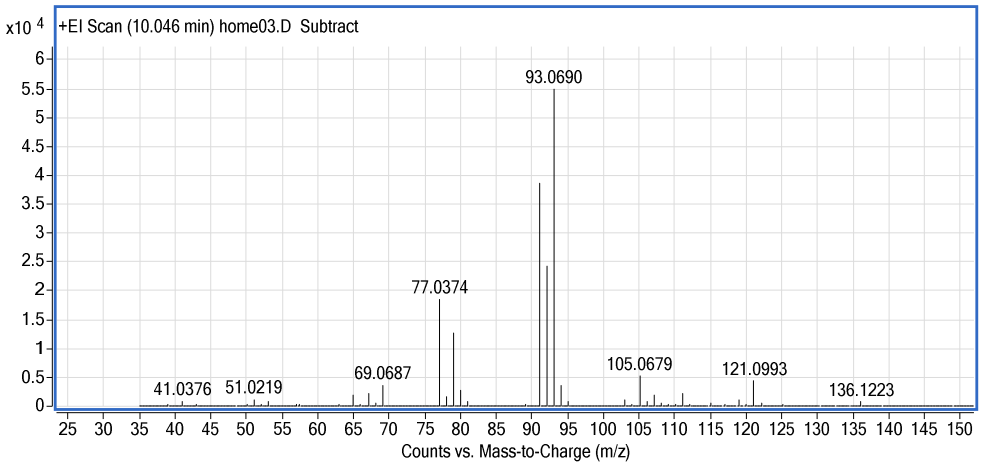


Figure 2-8. Mass spectra of *o*-xylene (a) from Home 03 and (b) from NIST MS library.

(a)



(b)

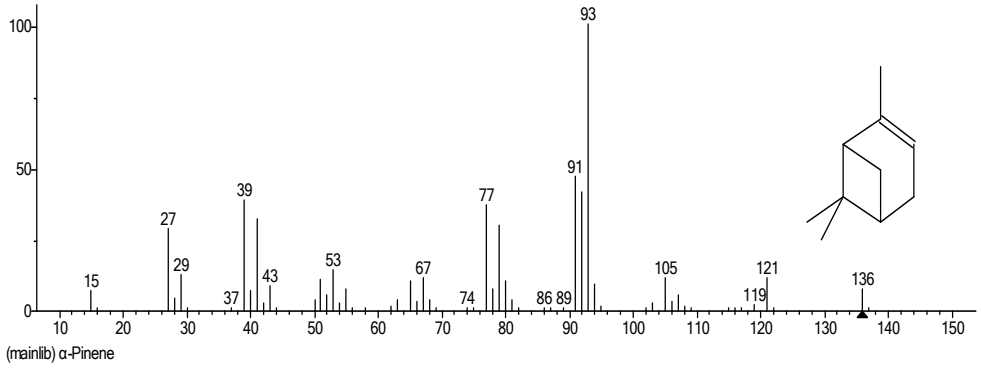
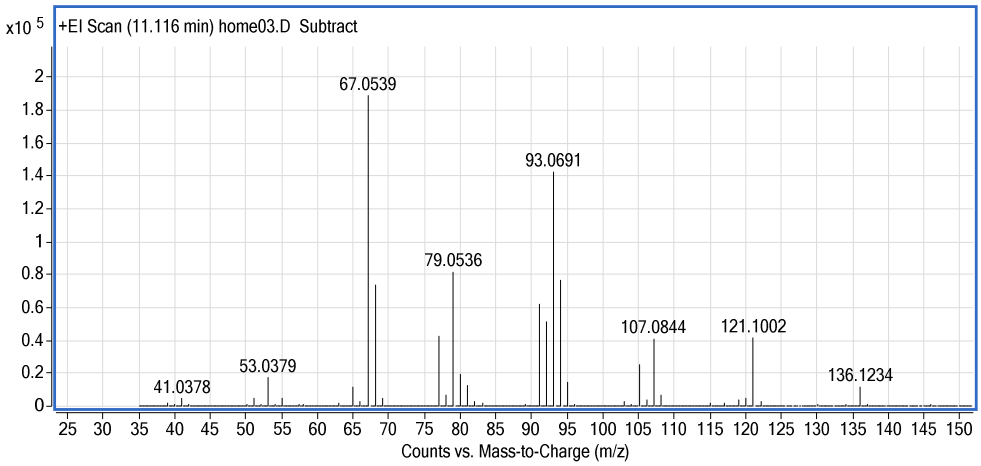


Figure 2-9. Mass spectra of *α*-pinene (a) from Home 03 and (b) from NIST MS library.

(a)



(b)

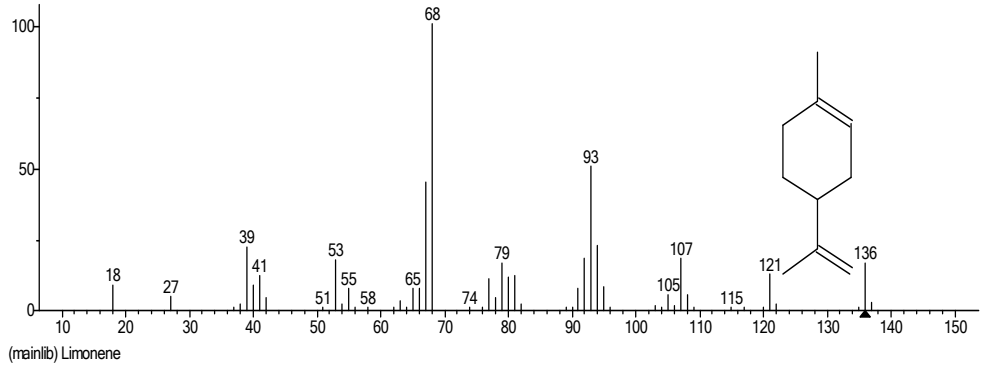
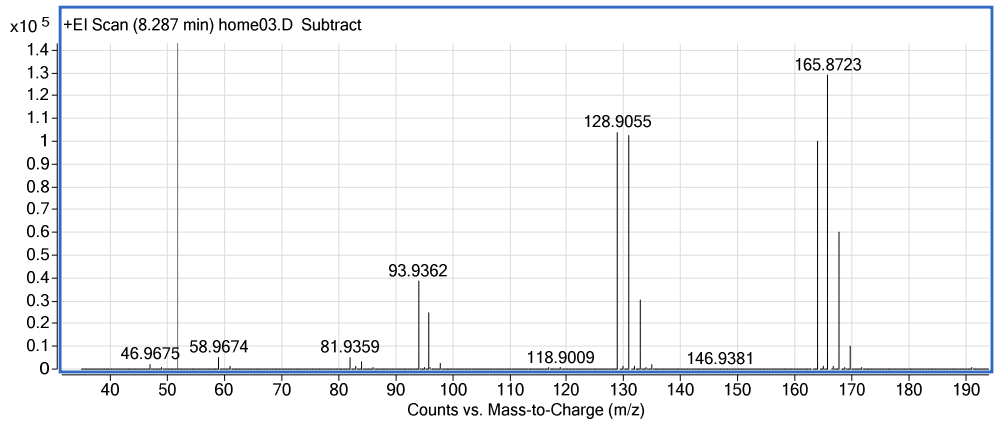


Figure 2-10. Mass spectra of d-limonene (a) from Home 03 and (b) from NIST MS library.

(a)



(b)

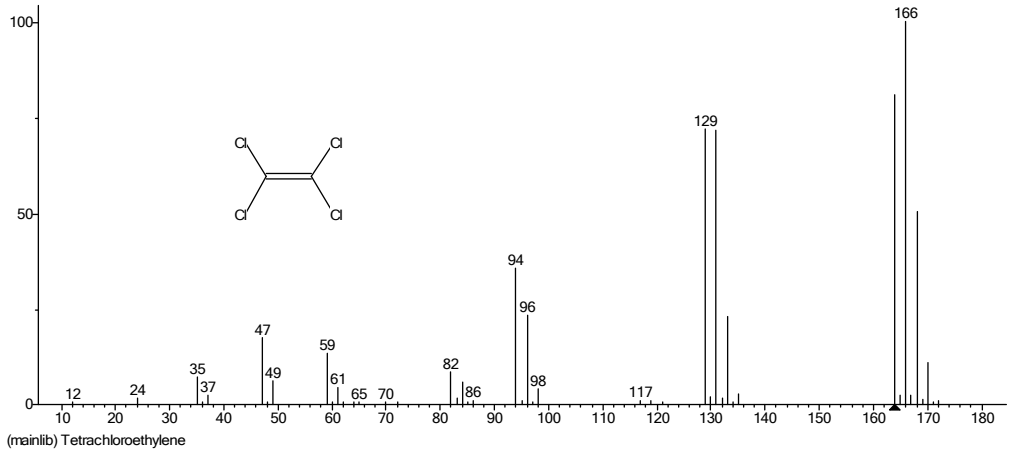
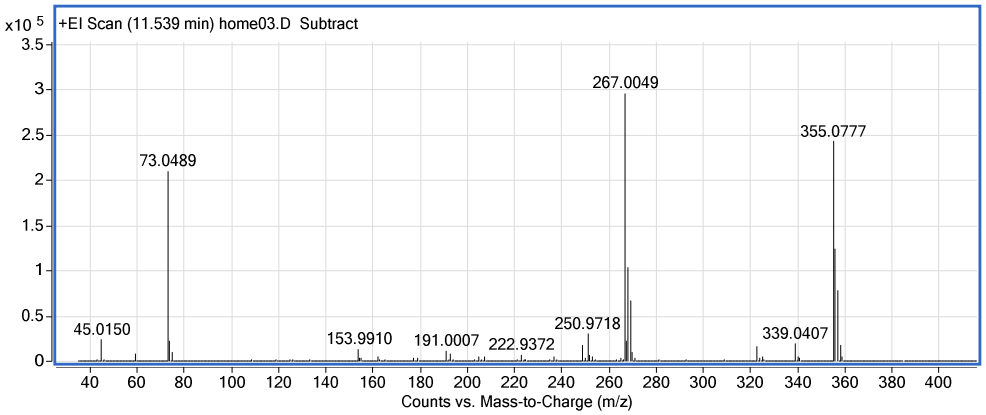


Figure 2-11. Mass spectra of tetrachloroethylene (a) from Home 03 and (b) from NIST MS library.

(a)



(b)

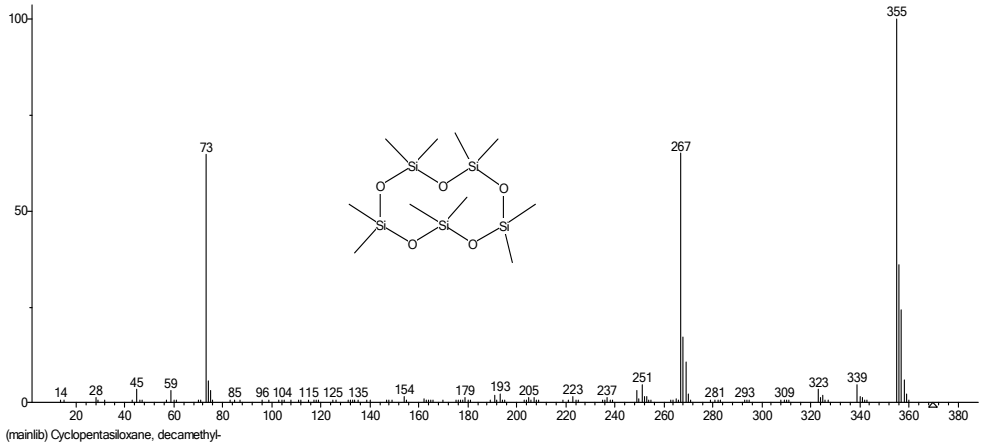


Figure 2-12. Mass spectra of D_5 (a) from Home 03 and (b) from NIST MS library.

Table 2.2. List of compounds and their base peaks in a TOF mass spectrum.

Compounds	Base peak (m/z)	Base peak formula	Theoretical exact mass (M_t)	Empirical exact mass (M_e)*	Difference $\lvert M_t - M_e \rvert$	Mass error $\lvert M_t - M_e \rvert / M_t * 10^6$ (ppm)
Isoprene	67	$C_5H_7^+$	67.0547	67.0533	0.0014	21
Benzene	78	$C_6H_6^+$	78.0470	78.0458	0.0012	15
Toluene	91	$C_7H_7^+$	91.0548	91.0550	0.0002	2
Ethylbenzene	91	$C_7H_7^+$	91.0548	91.0536	0.0012	13
m+*p*-xylenes	91	$C_7H_7^+$	91.0548	91.0536	0.0012	13
o-xylene	91	$C_7H_7^+$	91.0548	91.0535	0.0013	14
α-pinene	93	$C_7H_9^+$	93.0704	93.0690	0.0014	15
D-limonene	68	$C_5H_8^{+}\cdot$	68.0626	68.0611	0.0015	22
Tetrachloroethylene	164	$C_2Cl_4^+$	163.8754	163.8751	0.0003	2
Naphthalene	128	$C_{10}H_8^+$	128.0626	128.0608	0.0018	14
Hexamethylcyclotrisiloxane	207	$C_5H_{15}O_3Si_3^+$	207.0329	207.0332	0.0003	1
Octamethylcyclotetrasiloxane	281	$C_7H_{21}O_4Si_4^+$	281.0517	281.0538	0.0021	7
Decamethylcyclopentasiloxane	355	$C_9H_{27}O_5Si_5^+$	355.0705	355.0774	0.0069	19
Dodecamethylcyclohexasiloxane∇	429	$C_{11}H_{33}O_6Si_6^+$	429.0893	429.0909	0.0016	4

Percent error of the measurements by TOF/MS is ~10%.

*Empirical exact mass based on analysis of Home 03 from London.

∇m/z of 429 was not the base peak but was chosen as it was unique to the compound.

2.2.5 19-homes study in London

As part of an exposure assessment during a pregnancy study in London, static sampling units were installed in participants' homes with sensors to account for a number of environmental stressors (including VOC compounds via canister sampling) shown to impact pregnancy outcomes [130]. The sampling occurred in spring of 2015.

A questionnaire survey was conducted to collect further information about the homes sampled. Some of the information has been tabulated in Table 2.3. In summary, occupancy density ranged from 2-6 people in each home; 74 % of homes were double-glazed; 50% of homes had gas cooking; mean temperature values ranged from 19 ℃ to 26 ℃ and humidity from 30 % to 54 %. Indoor sampling took place in the living rooms of all the homes, with 32 % of the homes featuring an open-plan living room and kitchen. Household characteristics recorded for London houses mainly captured factors that can influence the concentration of VOCs generated indoors such as the building age, square footage of the homes, flat/house types, glazing of windows, occupancy densities, as well as the type of stoves installed in the kitchen.

VOCs samples were collected in evacuated canisters as described in Chapter 2.2.1. The canisters were packaged with passive air sampling inlet kits at ambient temperature and shipped from York to London. After sampling for about a week, the canisters from London were sent back to York at ambient temperature and analysed within 14 days.

Temperature and relative humidity measurements were conducted using an integral unit developed by the University of Cambridge Department of Chemistry, 'SNAQ Wireless sensor unit' [131]. The unit incorporated temperature and RH

probes with a logging interval set to 2 seconds. A GPRS transmitter stored and uploaded data to a server for post-processing and off-line analysis.

Table 2.3. Characteristics of sampled homes in London.

Homes	Occupancy	Placement	Windows glazing	Most abundant VOC
01	4	Living room	Double	α-Pinene
02	2	Living room and kitchen	Triple	d-Limonene
03	2	Living room and bedroom	Double	d-Limonene
04	3	Living room and kitchen	Single	d-Limonene
05	3	Living room	Double	α-Pinene
06	3	Living room and kitchen	Double	α-Pinene
07	4	Living room	Double	d-Limonene
08	4	Living room	Double	d-Limonene
09	3	Living room	Double	d-Limonene
10	3	Living room	Double	d-Limonene
11	4	Living room	Single	d-Limonene
12	2	Living room	Double	d-Limonene
13	2	Living room and kitchen	Double	d-Limonene
14	3	Living room and kitchen	Double	α-Pinene
15	3	Living room and kitchen	Single	α-Pinene
16	3	Kitchen	Single	d-Limonene
17	3	Living room	Double	d-Limonene
18	2	Living room	Single	d-Limonene
19	6	Living room	Double	Toluene

2.2.6 6-homes study in York

Six similar homes in York UK were chosen at random by BBC researchers as part of the programme “Trust me I’m a Doctor” broadcast in January 2016. Sampling was conducted in autumn of 2015. The selected homes were of 3 and 4 bedroom-size, built around 15 years ago. Three samples were taken in each home, and the time span between each sampling period was approximately two weeks. In a similar fashion to the London measurements VOCs samples were collected into evacuated 6-litre Silica-treated steel passivated canisters integrated over a week using constant flow critical orifice restricted inlets, and analysed within 14 days after sampling. The sampling canisters were placed in living rooms. In addition to canister sampling, formaldehyde sampling was performed at three of the homes, using a carbonyl derivatisation method with a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil® [132] (Radiello code 165, Supelco Analytical, USA) followed by HPLC analysis.

Information such as the types and frequency of consumer/cleaning products used were collected from each of the homes studied in York. In the homes studied, between six to ten different products were used in each home per week. The frequency of usage of each item ranged between one to ten times per week. We note that the types and frequency of product usage varied significantly from household to household; the types of products used included, general room fragrances, plug-in air fresheners, cleaning sprays and polishes, scented candles, and washing liquids as well as numerous different personal care products. None of the selected residences had attached garages and no indoor smoking activity was reported.

2.3 Results and analysis

The chromatograms obtained for the detection with TOF/MS and PID are as shown in Appendix A.

2.3.1 19-homes study in London

The most abundant and frequently detected VOCs in almost all UK homes were α-pinene and d-limonene. These originate from a combination of natural sources, including plants and foods, and from fragranced consumer products, a class that we define as including personal care and more general cleaning materials [133]. Compounds including toluene, ethylbenzene and xylenes which are constituents of household products i.e. paints, adhesives [134, 135] etc. were also ubiquitous. In a study by Liu et al., the concentration and source characteristics of carbonyls, benzene, toluene, ethylbenzene and xylenes in Beijing homes were studied with higher concentrations of some compounds (i.e. formaldehyde, acetaldehyde, benzene and toluene) attributed to the recent renovation of the homes [136]. In a different study by Xu et al., the measured VOCs (including alkanes, benzene, toluene, xylenes and terpenes) concentrations in the indoor environment were generally higher than that of the outdoor environment, with the exception of carbon tetrachloride [62]. Additionally, it was inferred that while compounds such as benzene and short-chain alkanes were likely to be from outdoor sources, compounds such as monoterpenes and naphthalene were likely to have originated from indoor sources [62]. In some of the London homes naphthalene was observed, although its origins could be from many different sources including cigarette smoke, pesticides and insecticides, or diesel fuel [137-139]. Known halogenated carcinogens such as 1,2-dichloroethane and tetrachloroethylene were observed in several homes. Cyclic volatile methyl siloxanes (cVMS) such as hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4) and

decamethylcyclopentasiloxane (D_5), were also detected frequently. These compounds are ubiquitous and can easily be found as background contamination in blank or control samples [71], resulting in persistently high background concentrations of cVMS found in our analyses. Although the concentrations of these cVMS were not quantifiable, their apparent high concentrations and wide occurrence indoors are highlighted here as a significant feature of UK homes.

The variability in the concentration of selected indoor VOCs for the 19 homes is shown in Figure 2-13. Figure 2-13 illustrates that certain VOCs within the London homes vary considerably, and no significant relationship was found to be associated with building age, size or occupancy. Whilst most VOCs show considerable variability between homes, the most abundant species observed are typically the monoterpenes, i.e. d-limonene and α-pinene. These compounds were observed in concentrations ranging from below the detection limit (0.01 µg m^{-3}) to as high as 54 µg m^{-3}. This is a 5-day average concentration and hence the short-term peak concentrations are likely to have been higher. It was inferred that the greater variability seen in monoterpenes, compared to other VOCs, likely reflects the heterogeneous daily habits of the inhabitants in their use of cleaning and personal care products. Given there are sources of d-limonene from food, plants and flowers it would be reasonable to consider that there is a 'natural' component to the observed variability and an anthropogenic component, although of course the definition is somewhat arbitrary. In the UK under wintertime conditions an outdoor natural source of monoterpenes from trees and plants can be considered negligible. Order-of-magnitude differences were seen in the average concentration of compounds such as toluene (factor of 19) and xylenes (factor of 26 for *o*-xylene) between homes in the study, with the least variability, a factor of 4, shown for benzene.

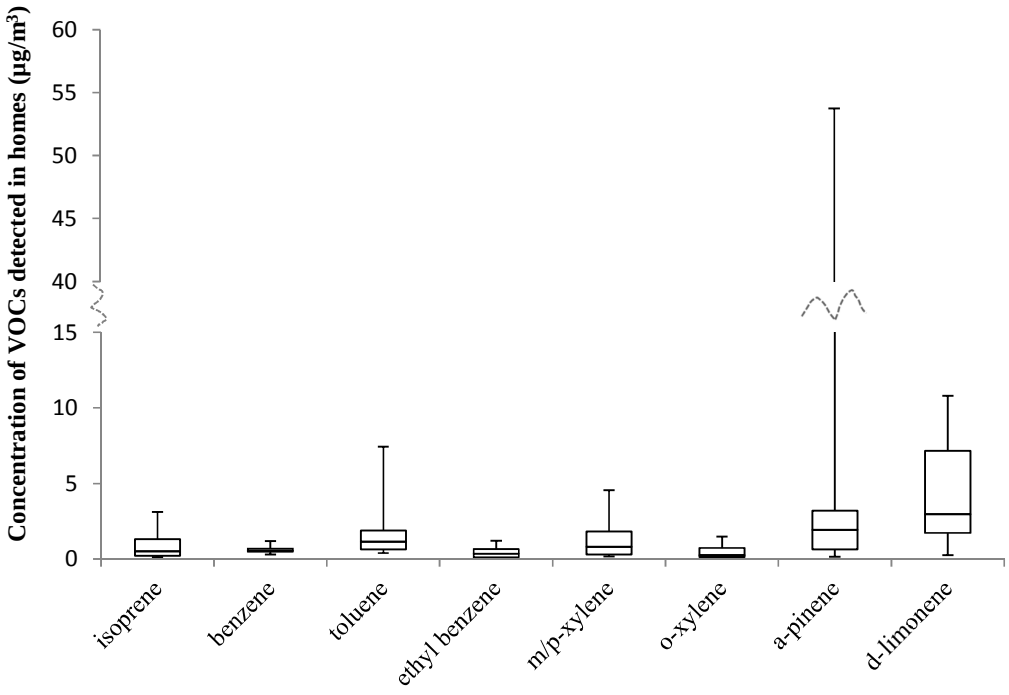


Figure 2-13. Averaged concentrations of the most abundant indoor VOCs from 19 homes in London showing the median, interquartile range, and the maximum and minimum values.

The indoor concentration of benzene is stated to be well-correlated with its outdoor concentrations, with the indoor/outdoor (I/O) ratio being close to 1 [140-143]. Hence, the variability in benzene concentrations observed in this study were taken to be a proxy for variation in outdoor concentrations and ventilation influences on the concentrations of the other compounds observed in each of the homes. The ratios of the concentrations of each of the compounds to the respective concentrations of benzene for each sampling point were calculated and averaged as shown in Table 2.4. The ratios obtained for d-limonene (mean: 8; median: 5) and α-pinene (mean: 6; median: 3) were of a greater magnitude when compared to

the other VOCs which had mean and median ratios of below 1 to 3. This indicated that the most likely source of the high concentrations of, and variability in, d-limonene and α-pinene was from indoor sources.

For comparison, the ratios of the concentrations of VOCs/benzene were calculated for the data obtained from the outdoor sampling in London conducted by Dunmore et al. [144] in winter and summer. Table 2.5 shows the ratios obtained for the analysis of the outdoor concentrations, averaged over the two seasons. The ratios obtained for the outdoor concentrations of limonene and α-pinene to that of benzene was observed to be about 0.2 and 0.3 respectively. In contrast with the much higher ratios obtained in the present indoor concentrations, this further illustrated the predominant indoor sources of limonene and α-pinene.

Table 2.4. Ratios of concentrations of VOCs / benzene.

	Compounds / Benzene ratios						
	Isoprene	**Toluene**	**Ethyl-benzene**	***m*+*p*-xylenes**	***o*-xylene**	**α-pinene**	**d-Limonene**
Mean	1.35	2.71	0.73	2.03	0.75	5.88	7.64
Median	1.20	1.99	0.54	1.25	0.46	2.55	5.16
Q_1	0.36	1.40	0.28	0.69	0.27	1.30	3.60
Q_3	1.65	2.97	1.01	2.55	0.88	5.28	12.11

*Q_1 is the middle value in the first half of the data set (first quartile).
**Q_3 is the middle value in the second half of the data set (third quartile).

Table 2.5. Ratio of outdoor concentrations of VOCs / benzene.

	Compounds / Benzene ratios						
	Isoprene	**Toluene**	**Ethyl-benzene**	***m*+*p*-xylenes**	***o*-xylene**	**α-pinene**	**d-Limonene**
Mean	0.20	2.53	0.47	0.64	0.46	0.34	0.17
Median	0.41	2.25	0.43	0.56	0.39	0.35	0.13

A comparison was made between the concentrations of various VOCs in homes with single glazed windows versus those with double glazed windows. In the absence of ventilation measurements from each house this was considered to be a proxy for air exchange. Previous analysis of the ventilation effects of changing single pane to double glazed windows in UK homes showed large effects on air infiltration. Average impacts in the study by Ridley et al. showed a reduction from 0.9 ach (air change per hour) to 0.64 ach when window types were swapped [145]. However, as seen from Figure 2-14, it was difficult to draw a relationship between the types of windows and the concentrations of VOCs observed. T- tests were conducted for all the compounds listed in the figure, and the results showed that there was no statistically significant difference ($\alpha = 0.05$) between the concentrations of the compounds in homes with single and double glazed windows, i.e. for benzene: $t = 0.59$, $p = 0.58$; for ethylbenzene: $t = -2.05$, $p = 0.057$ (most significant); for d-limonene: $t = -0.299$, $p = 0.772$ (least significant). Although the type of glazing may give a general idea about the ventilation in a home, further tests would have to be conducted utilising larger sample sizes for a more conclusive relationship to be inferred between the types of glazing in homes, ventilation rates (or tightness) of the buildings and concentrations of compounds found in the indoor environment. In addition, there was no information about whether or not the windows were opened. Also no information was available on the frequency of window opening and the impact of outdoor sources of traffic-related VOCs could not be assessed, since no immediate outdoor data were available in the current study.

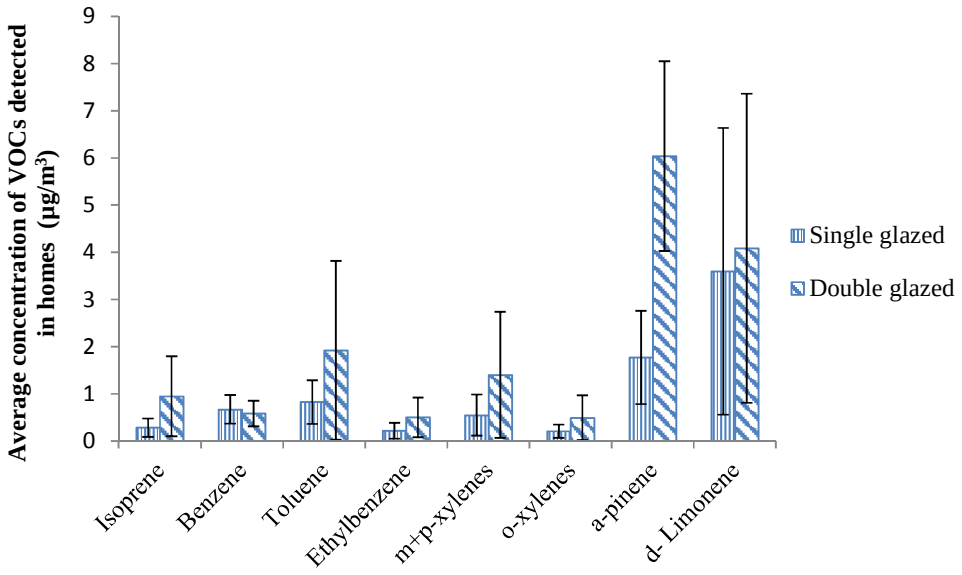


Figure 2-14. Comparison between homes with single-glazed windows and double-glazed windows.

2.3.2 6-homes study in York

The London results provided a single 5-day average sample snapshot across a range of houses. The York study was designed to examine the house-to-house variability for similar building types, albeit for a small sample size and period. This aimed to remove some of the variability induced by building construction and leave the predominant source of variability as occupant behaviour. Quantitative analysis was conducted for the same eight most abundant VOCs found in all homes. Similar to the results in London, the concentrations of α-pinene and d-limonene showed much greater variability and range compared to other VOCs (see Figure 2-17). 5-day averaged concentrations for α-pinene and d-limonene ranged from 2 to 229 µg m^{-3} and 18 to 1439 µg m^{-3} respectively, whereas concentrations for isoprene and benzene were within much narrower ranges of 11 to 22 µg m^{-3} and 7 to 19 µg m^{-3} respectively. An activity log (Table

2.6) kept by occupants in the 6 homes showed that the highest concentration of d-limonene found in Home 4, with a mean d-limonene concentration of 807 µg m^{-3}, was associated with occupants who used 9 different cleaning and fragrance products, each used on more than 10 occasions over the week. For other homes, 6-10 different products were used 1-5 times during the sampling period. Another interesting observation was that aside from Home 4 which had exceptional d-limonene concentrations, there were two further homes which exceeded mean d-limonene concentrations of 100 µg m^{-3} (Home 3 with a mean of 157 µg m^{-3}, and Home 6 with a mean of 111 µg m^{-3}). Although both homes used a variety of fragrances and cleaning products and with different and lower frequency of usage, they also burnt scented candles five times during the sampling period.

This large variability in concentrations of α-pinene and d-limonene within similar building-types highlighted the significant impact of inhabitant behaviour and indoor sources in each of the homes. It showed that whilst average estimated concentrations of species such as benzene are broadly representative of general exposure, more individualised measurements are vital for monoterpenes and mean values across a population study are not informative for individual exposure estimates.

Although both α-pinene and d-limonene are generally considered to have low toxicity [36, 146], they can form secondary pollutants by reaction with ozone and the hydroxyl radical, including compounds such as limonene oxide and formaldehyde [37, 147]. When concentrations of d-limonene are in the range 100-1000 µg m^{-3}, then secondary yields of products such as formaldehyde have the potential to become significant, relative to the expected indoor ambient concentrations of formaldehyde. The formaldehyde yield from the oxidation of d-limonene is around 10-19% [148] under typical outdoor atmospheric conditions, and so there exists at least the chemical potential for the formation of 10's of µg m^{-3} of

formaldehyde at steady state. This can be compared with the values of formaldehyde observed here which are of the same order of magnitude. The exact oxidative environment indoor is of course different to outdoors, but we would highlight that even relatively low yield reactions from monoterpenes would have the potential to make notable contributions to indoor formaldehyde when the primary VOC was in such high abundance. It has been demonstrated that indoor ozone-terpene reactions produces aldehydes such as formaldehyde [149]. Additionally, highly reactive hydroxyl radicals that are formed from ozone reactions [150] could further react with other compounds to form formaldehyde. Reaction mechanisms [68] of limonene with the hydroxyl radical and ozone to form formaldehyde are shown in Figure 2-15 and Figure 2-16 respectively.

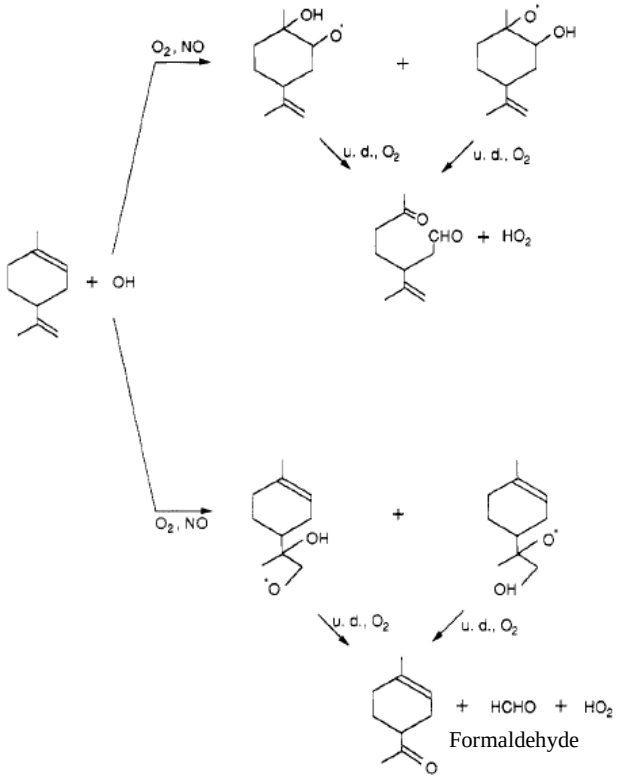


Figure 2-15. Reaction of limonene and OH [68].

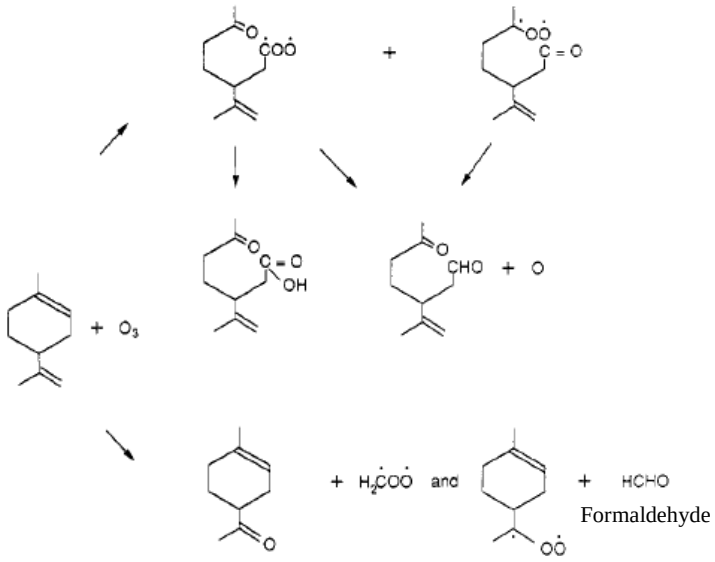


Figure 2-16. Reaction of limonene and ozone [68].

Formaldehyde was also measured in parallel in three homes (Homes 3, 4 and 5) in this study, taking the average measurement from pairs of co-deployed 72-hour average diffusion tubes. These three homes were chosen since they spanned the lowest to highest d-limonene concentrations. Average formaldehyde in Home 4, which reported the highest VOCs concentrations, was 66 µg m^{-3}, in Home 3 it was 47 µg m^{-3}, and in Home 5 which reported the lowest VOCs concentrations, it was 33 µg m^{-3}.

Figure 2-18 shows the data obtained for each individual home over a period of 3 weeks.

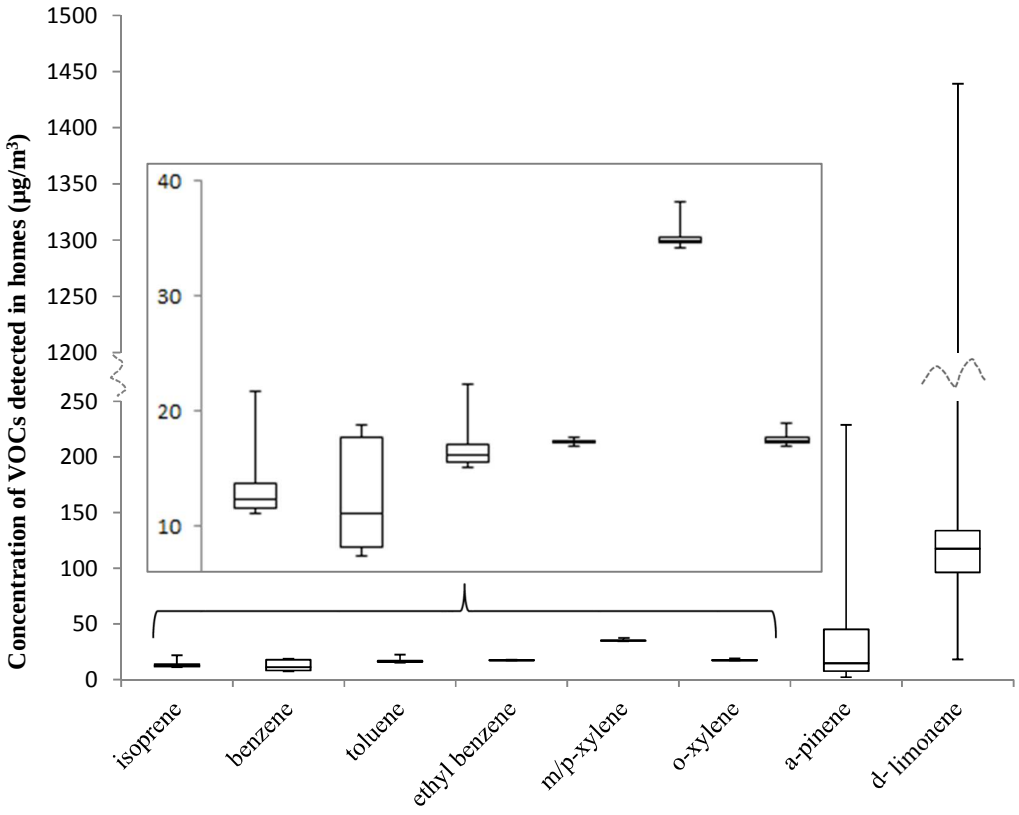


Figure 2-17. Averaged concentrations of the most abundant indoor VOCs from six similar build homes in York showing the median, interquartile range, and the maximum and minimum values.

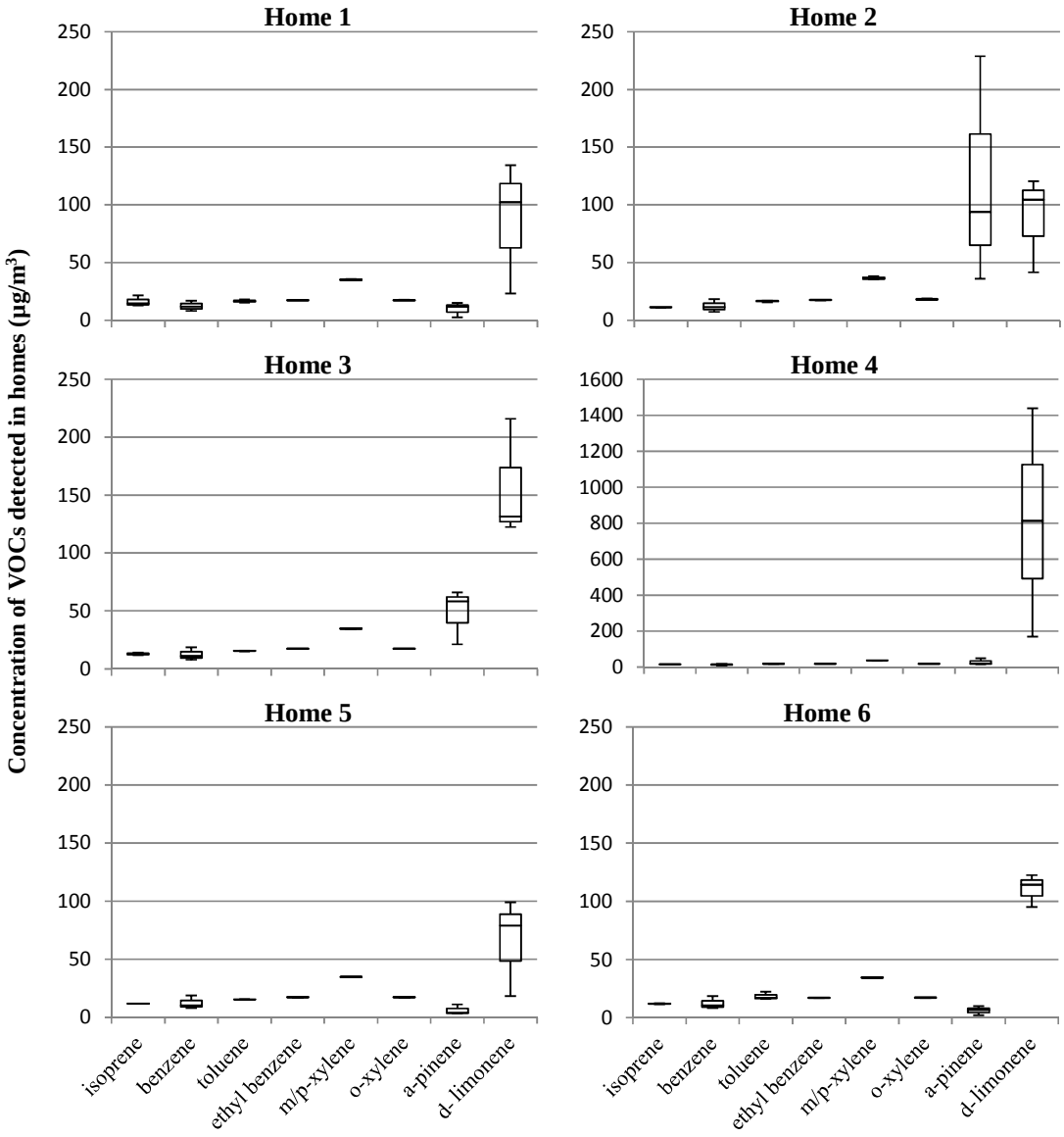


Figure 2-18. Variability in selected indoor VOCs of each of the homes in York, showing the median and the maximum and minimum values.

Table 2.6. Activity log for York homes.

	Type of consumer product	Quantity	Frequency used over sampling period
Home 1	Cleaning products	4	4 products used once
	Fragrance / freshener	2	2 products used 5 times
Home 2	Cleaning products	6	2 products used once; 4 products used twice
	Fragrance / freshener	1	1 product used 3 times
Home 3	Cleaning products	4	1 product used twice; 1 product used 3 times; 2 products used 5 times
	Fragrance / freshener	2	2 products used once
	Scented candle	1	1 product used 5 times
Home 4	Cleaning products	8	8 products used 10 times
	Fragrance / freshener	1	1 product used 10 times
Home 5	Cleaning products	8	4 products used once; 4 products used 5 times
	Fragrance / freshener	2	2 products used 5 times
Home 6	Cleaning products	5	5 products used 5 times
	Fragrance / freshener	1	1 product used 5 times
	Scented candle	1	1 product used 5 times

Similar to the data analysis for the London homes, the indoor/outdoor benzene concentrations were assumed to be ~1. The ratios of the concentration of each of the compounds to the respective concentrations of benzene observed in each of the homes in York were calculated and shown in Table 2.7. The ratios obtained for d-limonene were much higher, with a mean of 21 and median of 10, compared to the other compounds which have mean and median ratios of about 1 to 3. The ratios were also much higher when compared to the outdoor ratios of concentrations of α-pinene and d-limonene to that of benzene as shown in Table 2.5. Again, this pointed to predominant indoor sources of the monoterpene species.

Table 2.7. Ratios of concentrations of VOCs / benzene.

	Compounds / Benzene ratios						
	Isoprene	Toluene	Ethyl-benzene	*m*+*p*-xylenes	*o*-xylene	α-pinene	d-Limonene
Mean	1.17	1.50	1.57	3.17	1.58	3.28	20.75
Median	1.20	1.51	1.57	3.19	1.59	1.18	10.35
Q_1	0.79	0.94	0.98	2.06	1.02	0.47	7.26
Q_3	1.47	1.91	2.12	4.26	2.12	3.02	15.09

*Q_1 is the middle value in the first half of the data set (first quartile).
**Q_3 is the middle value in the second half of the data set (third quartile).

2.3.3 Comparison with other studies

Median concentrations of d-limonene observed in this work ranged from 79 µg m^{-3} to as high as 814 µg m^{-3}. While there was week-to-week variability within each of the homes sampled, the measured d-limonene concentrations were higher than any previously reported for homes in other studies. A previous national large survey conducted in 875 homes in England found that d-limonene values ranged from 0.1 µg m^{-3} to 308 µg m^{-3}, with a geometric mean of 6.2 µg m^{-3} [58]. In the AIRMEX (European Indoor Air Monitoring and Exposure assessment) study

involving VOCs measurements in public buildings, schools and homes in eleven European cities, d-limonene was identified as being predominantly derived from indoor sources, with mean concentrations of 9.4 µg m^{-3} and 29.2 µg m^{-3} and maximum concentrations of 176 µg m^{-3} and 493 µg m^{-3} observed in schools and homes respectively [151]. Studies in Detroit, Michigan, USA observed d-limonene with median and maximum concentrations of 16 µg m^{-3} and 173 µg m^{-3} [39], and 14 µg m^{-3} and 135 µg m^{-3} [152]. Similarly, 53 indoor environments in Ypsilanti, Michigan, USA showed d-limonene with median and maximum concentrations of 17 µg m^{-3} and 259 µg m^{-3} [59]. Another study of 22 homes in Puertollano, Spain observed d-limonene with median and maximum concentrations of 13 µg m^{-3} and 87 µg m^{-3} [60], while a study in Germany observed d-limonene with median and maximum concentrations of 16 µg m^{-3} and 65 µg m^{-3} [61].

2.4 Conclusions

This study identifies a common set of the most abundant VOCs found in 25 homes including benzene, toluene, xylenes, d-limonene and α-pinene, all classified in the European Commission INDEX strategy report as priority pollutants to be regulated [37]. Although substantial variability in the concentrations of all the top eight VOCs was recorded across the 25 homes, monoterpenes were clearly the most abundant and variable. In the London homes 68% had d-limonene as the most abundant VOC, and 26% α-pinene the most abundant. In the more modern energy efficient homes studied in York, the concentrations of d-limonene were as high as 1000 µg m^{-3}, associated with occupant behaviours of frequent use of cleaning and fragranced products. In at least one home the number of plug-in air fresheners used was likely beyond manufacturer's guidelines for use, although we do not have the original packaging information to confirm the advice given. It was observed that occupant behavioural patterns strongly influenced the

indoor concentration of monoterpenes to a much greater degree than any other class of VOCs. This was consistent with other studies [37].

The five-day averages recorded here would indicate that short-term transient concentrations of some VOCs may well regularly exceed part-per-million mixing ratios. At the very highest concentrations, and in the small number of homes where consumer products are used apparently in large quantities, there is at least the potential for ozone and hydroxyl reactions to generate secondary products including formaldehyde and aerosols under conditions with essentially unlimited feedstock of reactive carbon as monoterpenes [50]. The actual yields indoors remain very uncertain, and are not predicted here, but would be controlled by ozone ingress and interior photochemistry and surface reactions. Although canister sampling is very commonly used for outdoor regulatory VOC measurements [153] it is rarely used indoors. The study found the sampling methods to be compatible with a moderate size cohort study, straightforward for volunteer participants and compatible with their homes. The analytical method was characterised by low detection values in the part per trillion range, but the method sensitivity was rarely a limiting factor. In addition to some abundant hydrocarbon-based VOCs, a number of cyclic volatile siloxanes were seen in high amounts in all homes, but they could not be reported quantitatively due to high blank values in the analytical system.

Domestic indoor air cannot be easily regulated through public policies and the health impacts of exposure to monoterpenes may well be not be significant in the vast majority of homes. However a precautionary case could be made that better public information on fragranced product use would be worthwhile, with the objective to discourage behaviours that may in a small number of cases lead to unnecessarily excessive emissions in low ventilation domestic settings. This might

be achieved relatively simply through improved product labelling alongside more explicit advice on ventilation.

2.5 Acknowledgements

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Chapter 3

Indoor air analysis: Analysis of VOCs in new buildings during and after cleaning and use of fragrance products

3.1 Introduction

The quality of indoor air is important for the well-being and performance of an individual. There are a number of different factors that affects the indoor environment, and these include the immediate outdoor environment, use of chemicals and consumer products, and ventilation exchange rates. In recent decades, there have been initiatives for the conservation of energy that led to the construction of more energy-efficient buildings. This resulted in buildings with improved insulation and reduced ventilation, trapping pollutants and chemicals in the indoor environment [43, 44]. A study by Asere et al., in which four ventilation scenarios were assessed, concluded that different air exchange rates could have a significant impact on human productivity [154]. In another study by Wargocki et al., it was found that an increase in ventilation rates increased the occupants' satisfaction with the air quality and also led to an improvement in office tasks performances [155]. There is also evidence that an increase in ventilation rates is associated with the decrease in prevalence of Sick Building Syndrome (SBS) [156-158].

A study conducted by Järnström et al., which investigated the indoor air quality in newly built apartment buildings, found that the interior surfaces (floor, walls and ceiling) contributed to about 50% of the TVOC emissions in indoor air, suggesting the presence of other VOC sources [159]. It was also stated that the ceiling and PVC flooring were important contributors to VOC concentration levels [159]. In another study, it was observed that the high TVOC concentrations measured prior to occupancy in new apartment buildings generally decreased with time, but were increasingly replaced with other VOCs (i.e. β-pinene, d-limonene, 5-methyl-2-hexanol, and 3-methyl-2-pentanone) as the occupancy period increases [160].

This chapter describes the analysis of VOCs in two offices in a new building with different types of flooring: carpet and vinyl. Sampling was conducted under ventilated and non-ventilated conditions before occupants moved into the new building. Subsequently, cleaning products and fragrances were used under ventilated and non-ventilated conditions and air samples were collected for each scenario. Such activities were carried out to simulate occupancy in the new buildings whereby cleaning and scented products were used, and to identify the changes in VOC concentrations with the use of cleaning products and fragrances.

3.2 Test sites and conditions

6-liter canisters (SilcoCan, Thames Restek U.K. Ltd) were used in the sampling of air in two different locations in a new building: a vinyl-floored room and a carpeted room. A work flow diagram is shown in Figure 3-1. Prior to sampling, the canisters were evacuated with a vacuum pump. During sampling, canisters were attached to a pump and canisters were filled to 3 bar (see Figure 3-2). Samples were taken in both rooms with windows closed and windows opened at the beginning before any activities were carried out. Subsequently, samples were taken again before and after cleaning of a table top in the rooms, and again after the introduction of an air fragrance for an hour. These were carried out for 2 scenarios in which windows were closed and opened. Cleaning treatments were carried out with the aerosol cleaning agent “Pledge Furniture Polish Wood Classic” (Figure 3-3a). The aerosol was liberally sprayed onto the table top surface and cleaning was carried out for approximately 5 minutes. The air fragrance used was a plug-in scented oil, “Air Wick’s Life Scents Mom’s Baking Scented Oil” (Figure 3-3b), which was left to permeate the room at the highest intensity for an hour before air samples were collected. Table 3.1 lists the different samples collected across the different scenarios.

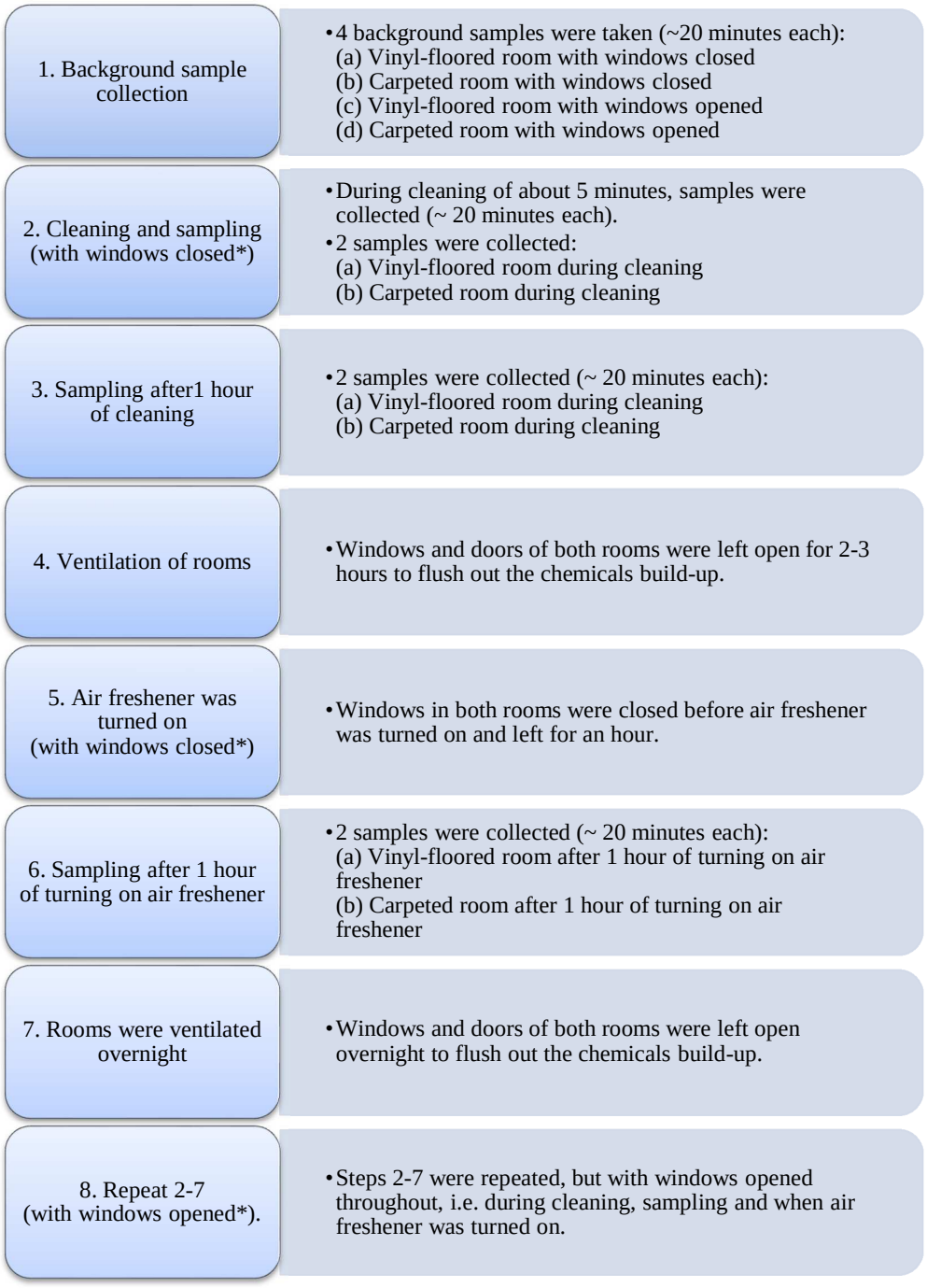


Figure 3-1. Work flow diagram of sampling carried out in new building.

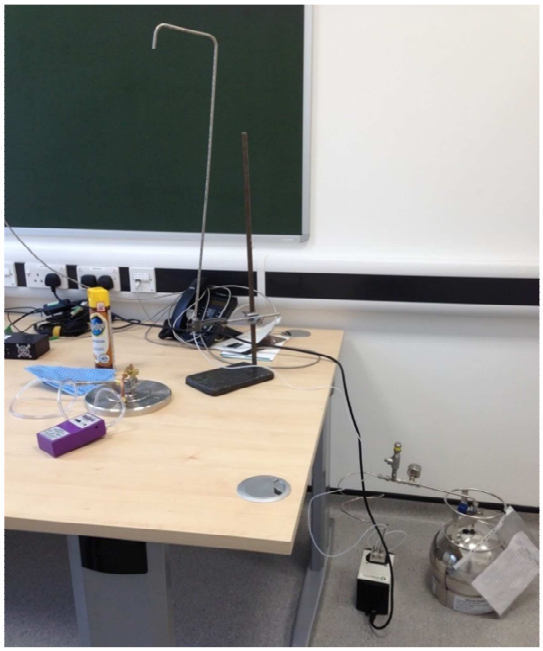


Figure 3-2. Canisters attached with pump for active sampling of indoor air.

Figure 3-3. (a) Cleaning product and (b) fragrance used.

Table 3.1. List of samples collected in new building.

No.	Flooring	Windows	Treatment
1.	Vinyl	Closed	NIL
2.	Carpet	Closed	NIL
3.	Vinyl	Opened	NIL
4.	Carpet	Opened	NIL
5.	Vinyl	Closed	During cleaning
6.	Vinyl	Closed	1h after cleaning
7.	Vinyl	Closed	1h after air fragrance
8.	Carpet	Closed	During cleaning
9.	Carpet	Closed	1h after cleaning
10.	Carpet	Closed	1h after air fragrance
11.	Vinyl	Opened	During cleaning
12.	Vinyl	Opened	1h after cleaning
13.	Vinyl	Opened	1h after air fragrance
14.	Carpet	Opened	During cleaning
15.	Carpet	Opened	1h after cleaning
16.	Carpet	Opened	1h after air fragrance

3.3 Thermal Desorption and GC instrumentation

The pressurised air sample was introduced into a thermal desorption unit (Markes Unity Series 2 Thermal Desorption Unit) prior to separation on the gas chromatography (GC) column. The gas was first passed through a cold-fingers set-up maintained at a temperature of about -35 ℃. This served to remove moisture from the gas before it enters the thermal desorption unit. 1000 mL of gas was sampled at 100 mL min^{-1}. The trap was purged for 1 minute at 100 mL min^{-1}

and heated from -30 °C to 300 °C at the maximum heating rate of the system and held for 3 minutes.

High purity helium (BIP Air Products, Keumiee, Belgium) was used as the carrier gas for GC. Separation was performed on a BPX5 column (50 m x 0.32 mm x 1.0 µm, length x internal diameter x film thickness) with two split outlets, one going to a time-of-flight/mass spectrometer (TOF/MS) and the other going directly into an olfactory port, used either for human assessment or as a mounting for a secondary photoionisation detector (PID) via a heated transfer line at a temperature of 200ºC. The oven was programmed to run at 40 °C for 3 minutes, then ramp at 15 °C min^{-1} to 125 °C, then at 20 °C min^{-1} to 250 °C and held for 2 minutes.

3.4 Results and Discussion

Comparisons were made among the different samples collected. Various graphs were plotted where V = vinyl-floored; C = carpeted; WC = windows closed; WO = windows opened.

Samples were collected before cleaning and the introduction of fragrances in the two rooms (Figure 3-4). Xylenes were the dominating VOCs with a total concentration of about 30 ng L^{-1} in either of the rooms when windows were closed. Xylenes are used as solvents in a variety of products such as paints, glues, inks, plastic and rubber, and could have been emitted from building materials such as carpet adhesives, vinyl cove adhesive, latex caulk, latex paint, and various mouldings [161]. α-Pinene had the next highest concentration of about 15 ng L^{-1} in either of the rooms when windows were closed. Emissions of α-pinene were likely to be from the wooden furniture such as the tables and the shelving that were newly installed.

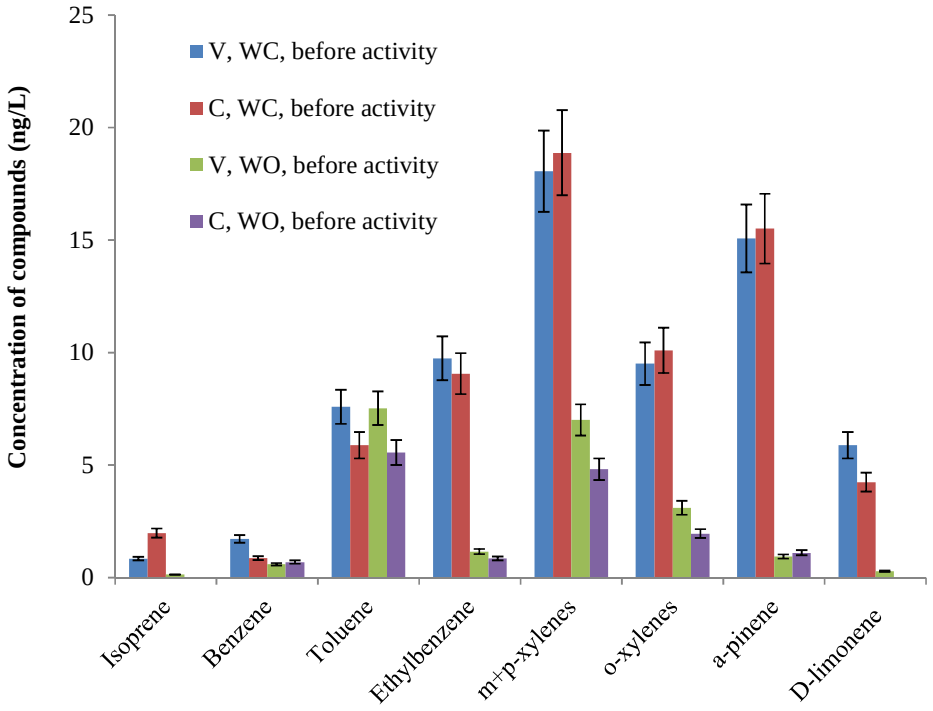


Figure 3-4. Concentrations of compounds before any activities were carried out. (V = vinyl-floored; C = carpeted; WC = windows closed; WO = windows opened)

Figure 3-5 and Figure 3-6 show the concentrations of the compounds during and after the various activities were carried out. It was observed that across the different scenarios, the concentration of compounds such as benzene, toluene and xylenes had a much lower variability compared to the concentration of compounds such as α-pinene and d-limonene. The range of concentrations observed were from 0.5 to 1.1 ng L^{-1}, 7.3 to 13.6 ng L^{-1}, 4.8 to 8.9 ng L^{-1} for benzene, toluene and *o*-xylene respectively, whereas the ranges were from below detection limit to 10.7 ng L^{-1} and 0.5 to 23.4 ng L^{-1} for α-pinene and d-limonene respectively.

These results further support the previous studies in UK homes that the usage of consumer products, such as fragrances and cleaning products, has a significant influence on the concentrations of a certain class of compounds, i.e. monoterpenes, in the indoor environment. The variability in the concentration of d-limonene was as high as a factor of 46, while that of benzene from combustion and transport, and solvents such as toluene and xylenes were much lower at 2.4 for benzene, 1.8 for toluene, and 1.8 for *o*-xylene.

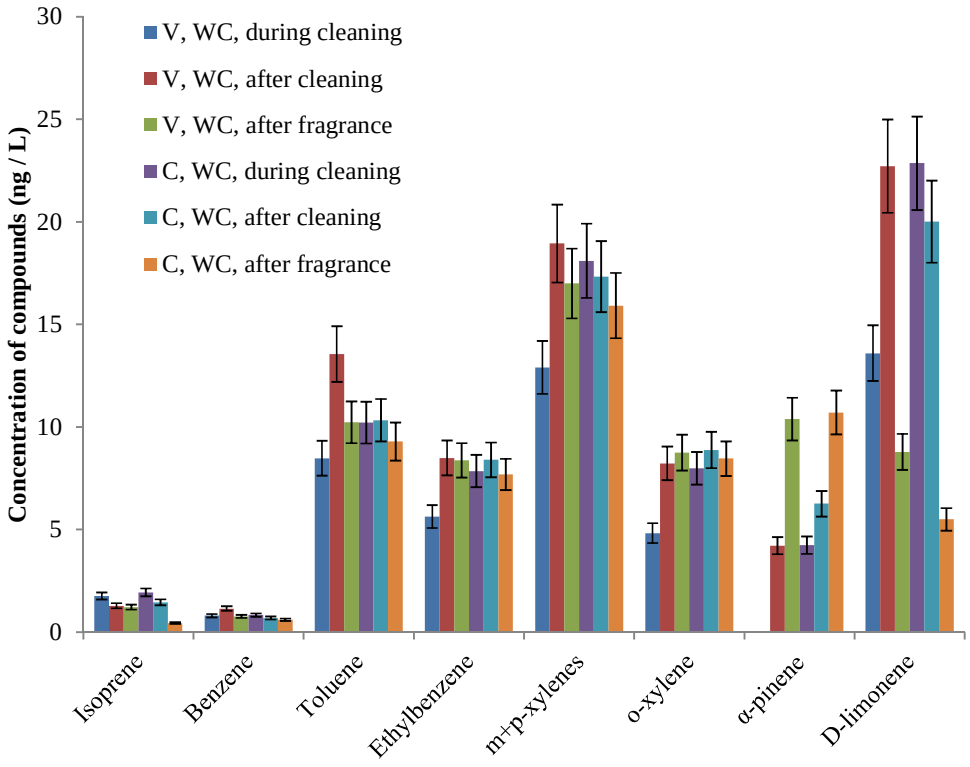


Figure 3-5. Concentrations of compounds detected across different scenarios in rooms with vinyl and carpet flooring when windows were closed. (V = vinyl-floored; C = carpeted; WC = windows closed; WO = windows opened)

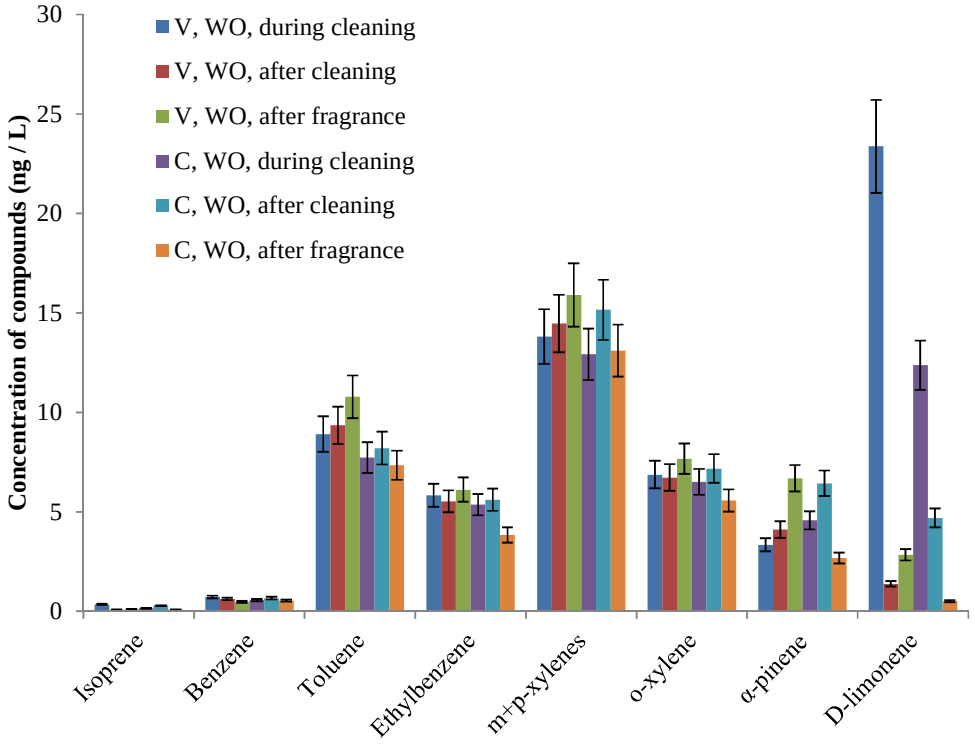


Figure 3-6. Concentrations of compounds detected across different scenarios in rooms with vinyl and carpet flooring when windows were opened. (V = vinyl-floored; C = carpeted; WC = windows closed; WO = windows opened)

Comparisons between the concentrations of benzene and d-limonene were made for the difference scenarios (Figure 3-7 to Figure 3-12). Benzene and d-limonene were the chosen compounds for this comparison study as benzene indoors was likely to be from outdoor sources and d-limonene was mainly to have originated from indoor sources.

From Figure 3-7 and Figure 3-8, with the windows closed (no ventilation) the concentrations of d-limonene in the rooms remained high or increased when samples were collected 1 hour after the cleaning activity. An increase in the concentration of d-limonene was observed in the vinyl-floored room after an hour

of cleaning, whereas there was a seemingly slight decrease observed in the carpeted room after an hour of cleaning. This could be due to the deposition of compounds onto the carpet surfaces, resulting in lesser amounts present in the air.

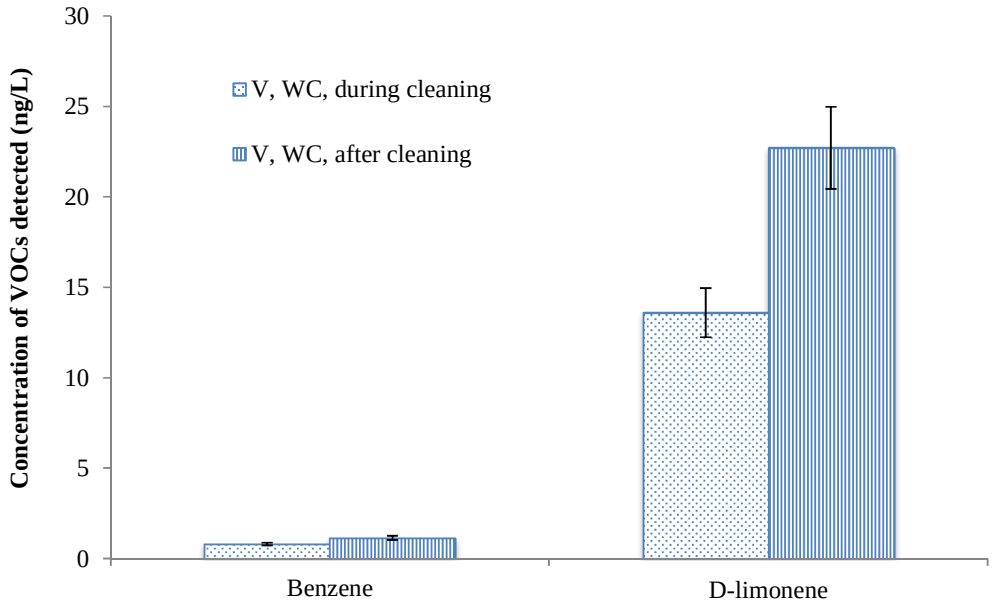


Figure 3-7. Concentrations of compounds in vinyl-floored room with windows closed during and after cleaning. (V = vinyl-floored; WC = windows closed)

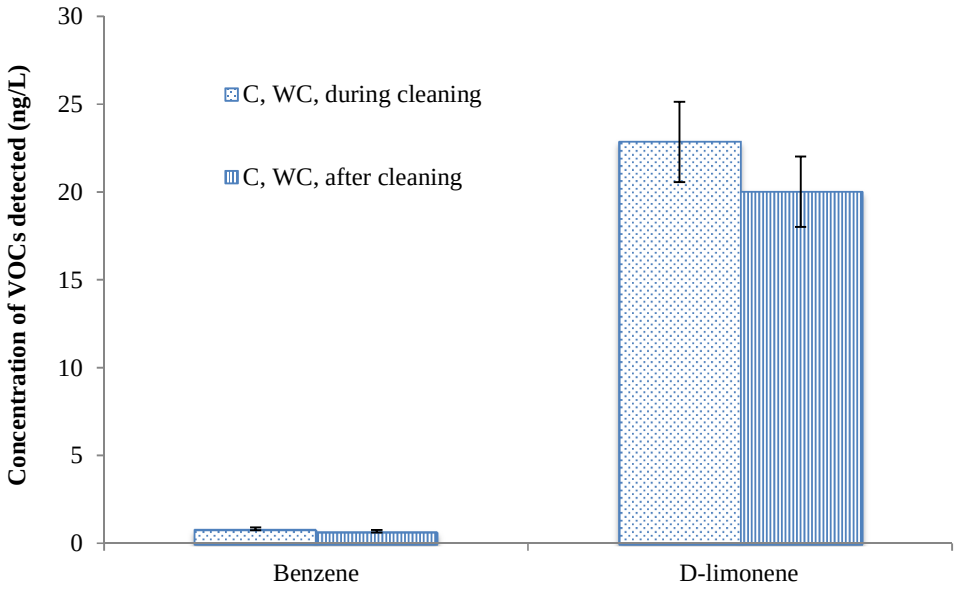


Figure 3-8. Concentrations of compounds in carpeted room with windows closed during and after cleaning. (C = carpeted; WC = windows closed)

As seen from Figure 3-9 and Figure 3-10, there was a significant decrease in the amount of d-limonene detected after 1 hour of cleaning when windows were left opened. With ventilation, the compounds found in the cleaning agent did not build up in the indoor environment and would allow for return to normalcy at a faster rate.

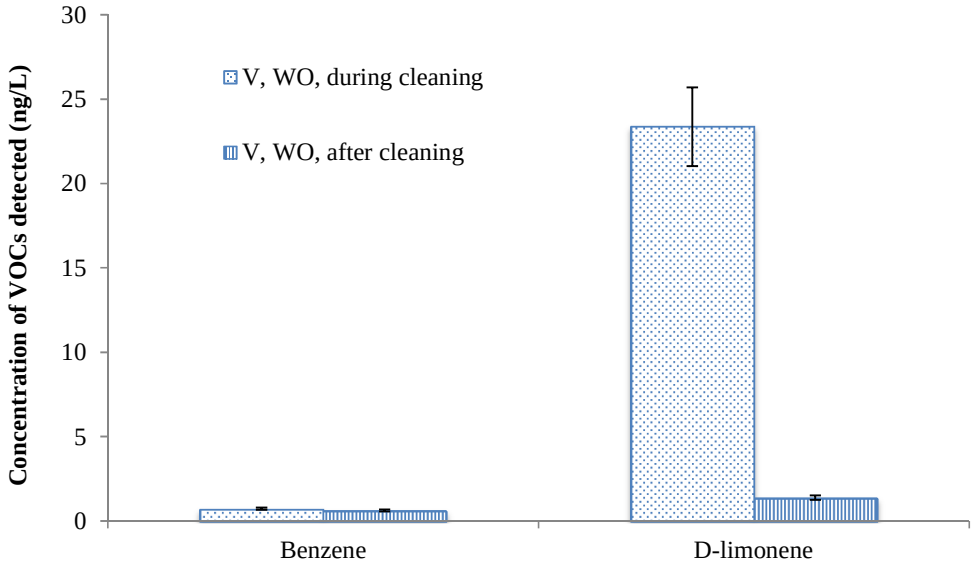


Figure 3-9. Concentrations of compounds in vinyl-floored room with windows opened during and after cleaning. (V = vinyl-floored; WO = windows opened)

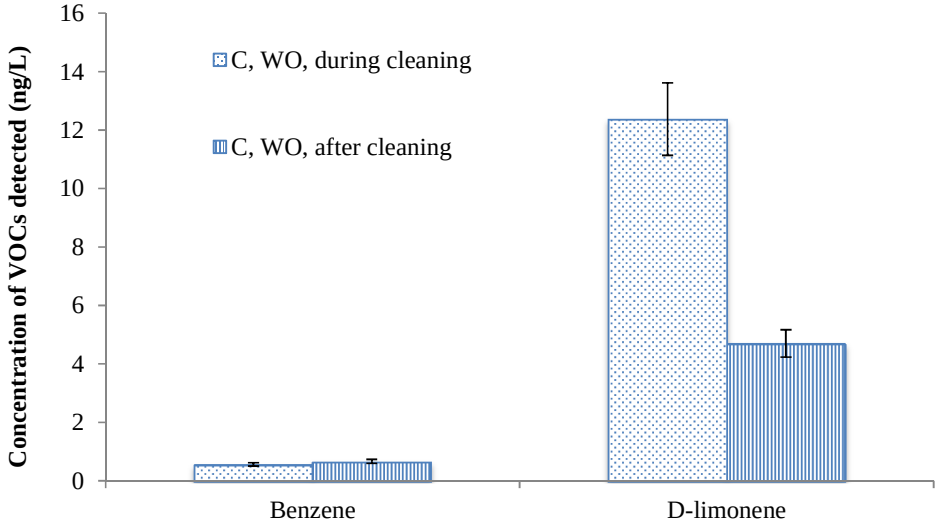


Figure 3-10. Concentrations of compounds in carpeted room with windows opened during and after cleaning. (C = carpeted; WO = windows opened)

In both the vinyl-floored and the carpeted rooms, concentrations of d-limonene detected were significantly lower when the windows were left opened during the application of the fragrance as seen in Figure 3-11 and Figure 3-12.

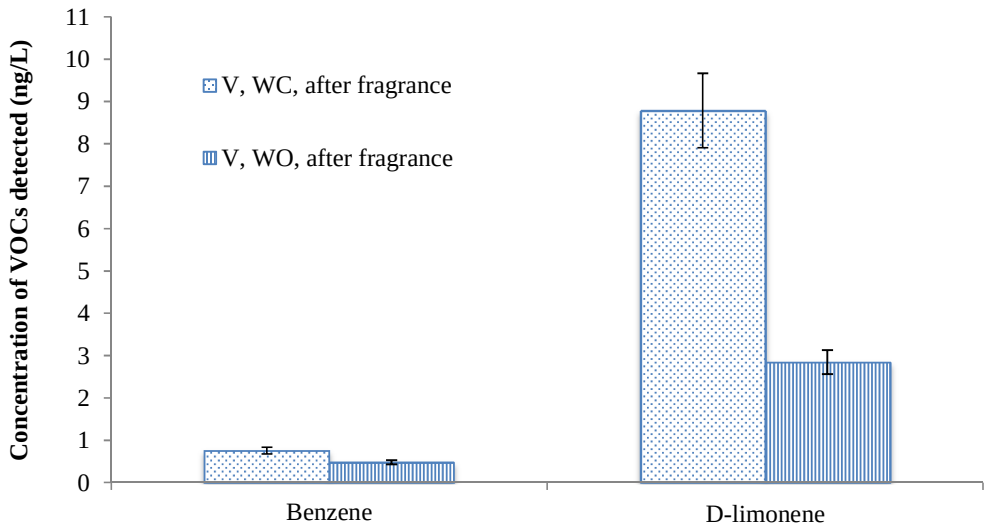


Figure 3-11. Concentrations of compounds in vinyl-floored room with windows closed and opened after application of air fragrance. (V = vinyl-floored; WC = windows closed; WO = windows opened)

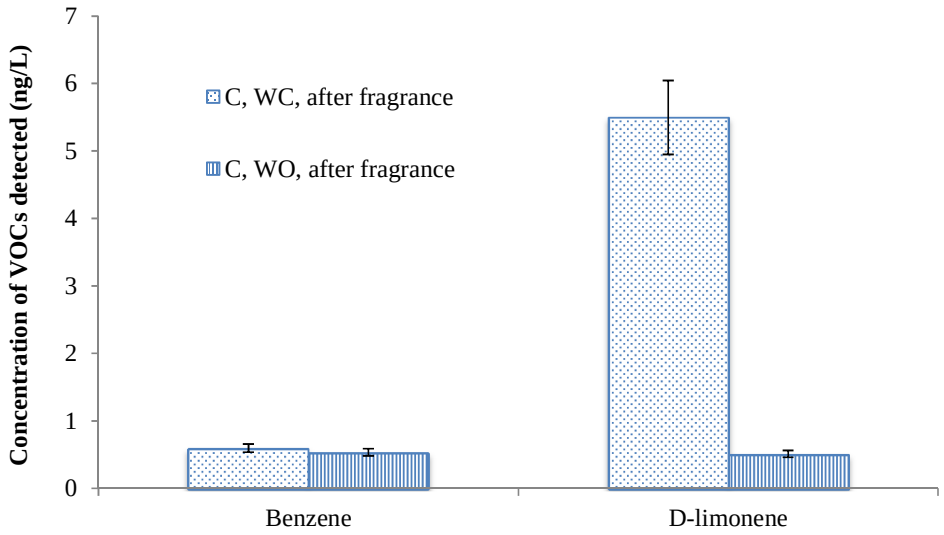


Figure 3-12. Concentrations of compounds in carpeted room with windows closed and opened after application of air fragrance. (C = carpeted; WC = windows closed; WO = windows opened)

3.5 Conclusion

This set of experiments generally shows that having simple ventilation measures i.e. opening of windows will allow for better air exchange and prevent the build-up of chemicals within an enclosed space. The reduction of d-limonene concentrations, after using fragranced cleaning products containing the aforementioned chemical, was observed when windows were left opened during and after the cleaning activity. The fluctuations in the d-limonene concentrations were evident when compared to that of benzene. Similarly, the application of air fragrance also resulted in a higher concentration of d-limonene observed when windows were closed, compared to when the windows were opened.

Chapter 4

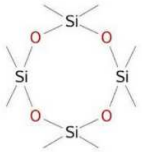
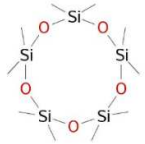
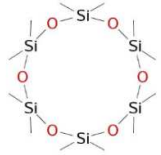
Sampling and analysis of cyclic volatile methyl siloxanes in air

4.1 Introduction to Cyclic Volatile Methyl Siloxanes

The study of Howard and Muir has provided an overview of emerging persistent and bioaccumulative chemicals that have been produced in commercial quantities [73]. Chemicals in this overview were considered to be bioaccumulative if they had high octanol-water partition coefficient ($logK_{ow}$) values, and persistent if their atmospheric oxidation half-life ($AO_{t1/2}$) was of the order of days, meaning as a consequence that they are potentially susceptible to regional or long-range atmospheric transport. A high air-water partition coefficient ($logK_{aw}$) coupled with a relatively low octanol-air partition coefficient ($log\ K_{oa}$) also is a good indication that the chemical is likely to be found in the air [162].

Cyclic volatile methyl siloxanes (cVMS) (see Table 4.1 for more information) have been widely used in a variety of consumer products such as fragrances, deodorants, cleaning products and lotions [69]. They are used as solvents or ingredients in formulations because of their volatility and smooth feel to the consumer. They also have important product performance qualities such as being inert, odourless and colourless, and therefore they are ideal for use as a solvent or main component in personal care products [81]. Octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) have been identified as chemicals that are in high volume production (range ~ 45×10^6 – 226×10^6 kg/yr) and which are potentially bioaccumulative ($log\ K_{ow}$ values of 5.09 and 5.71 respectively) and persistent ($AO_{t1/2}$ of 7.15 and 8.94 days respectively) [73]. Studies have also found cVMS to be large contributors to indoors VOCs [83, 163, 164] and hence it was of great interest to analyse such compounds in parallel to the indoor air analyses carried out.

Table 4.1. Information on cyclic volatile methyl siloxanes.

Name	Structure	Abbreviation	CAS	Formula	Molecular mass
Hexamethylcyclotrisiloxane		D_3	541-05-9	$C_6H_{18}O_3Si_3$	222.46
Octamethylcyclotetrasiloxane		D_4	556-67-2	$C_8H_{24}O_4Si_4$	296.62
Decamethylcyclopentasiloxane		D_5	541-02-6	$C_{10}H_{30}O_5Si_5$	370.77
Dodecamethylcyclohexasiloxane		D_6	540-97-6	$C_{12}H_{36}O_6Si_6$	444.92

The toxicity and persistence of tile coating products containing alkylsiloxanes were evaluated in a 2014 study which showed that the patients / study subjects exposed to those products developed symptoms such as coughing, chest pain and fever within a few hours [165]. Potential acute health effects of cVMS have also been discussed in other publications [69, 71].

A diurnal trend in cVMS atmospheric concentrations has been observed, with night-time samples having a higher average than day-time samples [81]. It was suspected that this phenomenon may be partly a result of the fluctuations of the planetary boundary layer and resulting atmospheric dilution. In the same study, it was also reported that indoor concentrations of cVMS were higher than those found outdoors. A connection between indoor concentrations and building occupancy was made. This was in agreement with a study of indoor air of different buildings with different occupant densities which concluded that cVMS, together with other volatile organic compounds (VOCs), were present in higher concentrations when there were more occupants per unit area [80]. There have in total however been rather few publications or measurements of cVMS in indoor air. Some studies have been conducted for outdoor air [75, 77, 162] and on the modelling of the concentration distributions of certain cVMS [166, 167]. The limited work on indoor air measurements and modelling of cVMS results in a rather poor knowledge of the individual source strengths for cVMS and the range of distribution that may now be present in the built environment. The indoor environment is however the location where concentrations are at the highest and where the sources are located – largely and perhaps solely anthropogenic. In terms of speciation, previous studies have also shown D_5 as the most prevalent cVMS found in samples ranging from personal care and household products to air samples of indoor and outdoor air [69, 71, 77, 80, 81].

Detection and analysis of cVMS in air samples have been typically made using gas chromatography – mass spectrometry (GC-MS) [75, 77, 80, 81, 162]. However the use of this analytical method may be more challenging than expected due to persistent high background concentrations of cVMS, including integral parts of the gas chromatograph that are susceptible to cVMS contamination. Inlet septa and capillary columns contain silicone and bleeding of these sources may result in false positives during analysis [71]. The handling of any part of the GC inlet or column system creates the potential for human contamination. Inlet septa contamination is less of an issue in air sample analysis, as thermal desorption is the most common inlet when the GC-MS is employed. Cyclic fragments of siloxane resulting from column bleed of siloxane based stationary phases can never be completely eliminated, but have been determined to be only a minor source of contamination [71].

One of the challenges faced in any sampling strategy to evaluate indoor exposure is quality assurance and quality control. cVMS are ubiquitous and can easily be found as background contamination in blank or control samples. In the methods reported by Yucuis et al., glassware used in the analysis was heated up to 450 °C overnight while other sampling components were rinsed thoroughly with solvents before use; ENV+ cartridges that were used as sorbents for cVMS analysis were also treated with relevant solvents and wrapped in aluminium foil before they were used [81]. ENV+ is a hyper crosslinked hydroxylated polystyrene-divinylbenzene copolymer with very high surface area. ENV+ is very versatile; it can retain a broad range of analytes with different polarity. The structure for this highly retentive non-polar SPE phase can be seen in Figure 4-1 [168]. Sampling was also carried out in parallel in to ensure repeatability of the method.

Some initial testing also involved the use of ABN sorbent. ABN is a modified polystyrene-divinylbenzene polymer that contains both hydrophobic and

hydrophilic groups, hence allowing for the extraction of analytes with a wide range of polarity. The sampling and extraction efficiency of ENV+ was compared with ABN to determine the better sorbent to be used for the analysis of cVMS. The ABN sorbent used in this work has a particle size of about 50 µm, compared to ENV+ which has a particle size of about 90 µm. It was to be explored if the larger surface area to volume ratio of ABN would result in a higher extraction efficiency. The structure of ABN can be seen in Figure 4-2 [169].

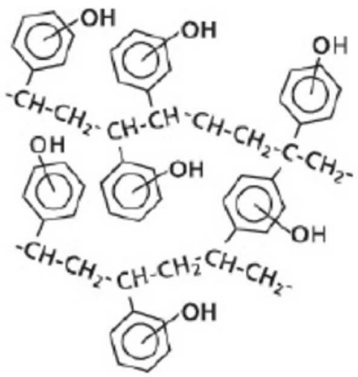


Figure 4-1. ENV+ polymer.

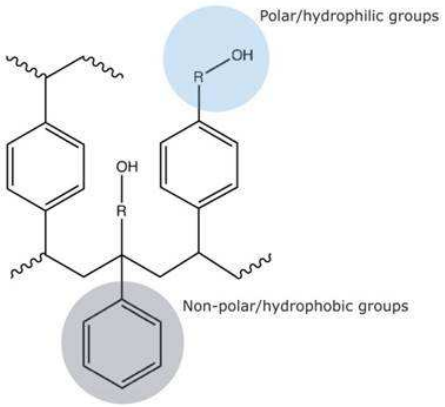


Figure 4-2. ABN polymer.

ENV+ cartridges have been used in some of those studies reviewed earlier [75, 81, 162]. In these studies samples were actively collected with pumps were attached to the cartridges via PTFE tubing and air pulled through the cartridges during sampling. Every sample cartridge was accompanied by a blank and another cartridge set up in parallel to check for and ensure repeatability of the extraction method. Prior to sampling, the cartridges were prepared to reduce the contamination of cVMS on them. Isotope standards (^{13}C-D_5) were used as internal standards and for calibration. The samples were then eluted using n-hexane.

Prior to extraction, the cartridges were prepared and processed to reduce the contamination of cVMS on them. Isotope standards (^{13}C-D_5) were used as internal standards and for calibration. The samples were then eluted using n-hexane. It was thought that these procedures used by Kierkegaard and McLachlan [162] could be emulated or used as a reference.

4.2 Internship in ACES, Stockholm University

In view of the above mentioned work, further research and measurements for indoor cVMS was of interest. Indoor air samples could be collected and measurements of the amount of cVMS could be made. An internship was arranged with ACES, Stockholm University. The aim of the internship was to learn the active sampling method using ENV+ cartridges and how to deal with the contamination issues faced when dealing with cVMS given their prevalence in the surroundings. Tetrakis(trimethylsiloxy)silane (M4Q) was used as the internal standard as it is chemically similar to the cVMS of interest. A structure of M4Q is shown in Figure 4-3.

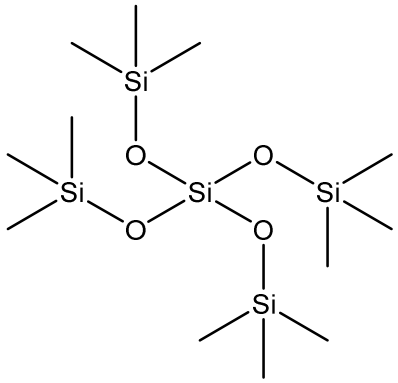


Figure 4-3. Structure of M4Q.

A passive sampling method was also developed during the research period in Stockholm, and this method was brought back to York and further studies were conducted.

4.3 Materials

For the work conducted in Stockholm, octamethylcyclotetrasiloxane (D_4) (Fluka, purity >99%), decamethylcyclopentasiloxane (D_5) (Fluka, purity >97%) and tetrakis(trimethylsiloxy)silane (M4Q) (purity 97%) were purchased from Sigma-Aldrich Sweden AB, while dodecamethylcyclohexasiloxane (D_6) was purchased from Flurochem Ltd., UK. Dichloromethane (DCM) and *n*-hexane (both lichrosolv quality) were purchased from Merck (Darmstadt, Germany). Solid phase extraction (SPE) cartridges, Isolute ENV+ (hydroxylated polystyrene-divinylbenzene copolymer) and ABN (modified polystyrene-divinylbenzene polymer) were obtained from Biotage AB (Uppsala, Sweden).

For the work conducted in York, hexamethylcyclotrisiloxane (D_3) (purity 98%), octamethylcyclotetrasiloxane (D_4) (purity 98%), decamethylcyclopentasiloxane (D_5) (purity 97%), dodecamethylcyclohexasiloxane (D_6) (purity 97%) and tetrakis(trimethylsiloxy)silane (M4Q) (purity 97%) were purchased from Sigma-

Aldrich Co. Ltd. Dichloromethane (DCM) and *n*-hexane (both lichrosolv quality) were purchased from Merck Millipore. Isolute ENV+ (hydroxylated polystyrene-divinylbenzene copolymer) were obtained from Biotage AB (Uppsala, Sweden).

In both York and Stockholm, polyamide fabric (Sefar Nitex PA 6.6) was purchased from Sefar Ltd.

4.4 Instrumentation

All analyses in Stockholm University were performed using a GC-MS with electron ionisation. The GC (Trace GC Ultra, Thermo Electron Corp.) was equipped with a large-volume splitless injector with a Merlin microseal septum. 5 µL of sample or standard extract was injected at an injector temperature of 220 °C. The analytical column was a 30 m TG-5SILMS (0.25 mm i.d., 0.25 µm film thickness, Thermo Scientific), with a 5 m retention gap of deactivated fused silica was used (0.32 mm i.d., Agilent Technologies). The carrier gas was helium (99.995 %, AGA, Stockholm, Sweden). The oven was programmed to run at 40 °C for 1.5 minutes, then ramped at 10 °C min^{-1} to 150 °C, the ramped at 30 °C min^{-1} to 300 °C and held for 5 minutes. The transfer line was kept at 250 °C and the ion source at 200 °C. The ions monitored were *m/z* 207 and 208 for D_3, *m/z* 281 and 282 for D_4, *m/z* 355 and 356 for D_5, *m/z* 429 and 430 for D_6, and *m/z* 281 for M4Q.

The analyses in York were carried out on a GC-TOFMS using electron ionisation. The GC (Agilent 7890B) was equipped with a Gerstel septumless sampling head. 1 µL of the extract was injected at an initial injector temperature of 150 °C, ramped at 12 °C min^{-1} to 220 °C. High purity helium (99.999 %, BIP Air Products, Keumiee, Belgium) was used as the carrier gas for GC. Separation was performed on a BPX5 column (50 m x 0.32 mm x 1.0 µm, length x internal diameter x film thickness). The oven was programmed to run at 40 °C for 2 minutes, then ramp at

10 °C min^{-1} to 150 °C, then at 20 °C min^{-1} to 250 °C and held for 5 minutes. The ions monitored were *m/z* 207 for D_3, *m/z* 281 for D_4, *m/z* 355 for D_5, *m/z* 429 for D_6, and *m/z* 281 for M4Q.

Figure 4-4, Figure 4-5 and Figure 4-6 show the extracted ion chromatographs for the analyses carried out in Stockholm and York respectively.

Figure 4-6, in particular, shows the extracted ion chromatograms at the exact masses of the ions, allowing for the unequivocal identification of the compounds in this study. A tabulated data of the exact mass extracted ion analysis of cVMS with TOF/MS is shown in Table 4.2. The actual mass spectra of D_3, D_4, D_5, D_6 and M4Q are compared with that of the library as shown in Figure 4-7 to Figure 4-11.

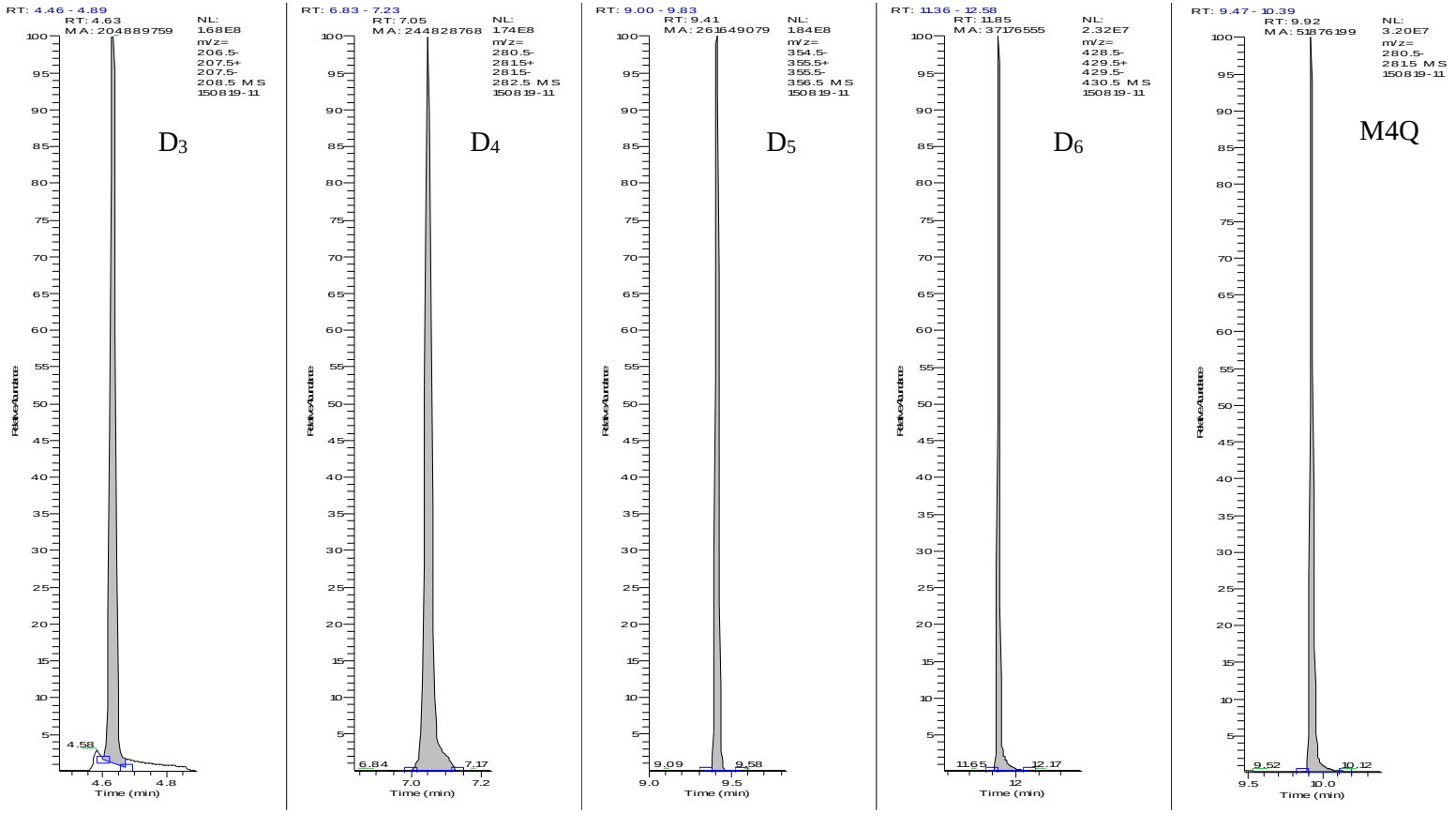


Figure 4-4. Extracted ion chromatographs of D_3, D_4, D_5, D_6 and M4Q for the analyses carried out in Stockholm.

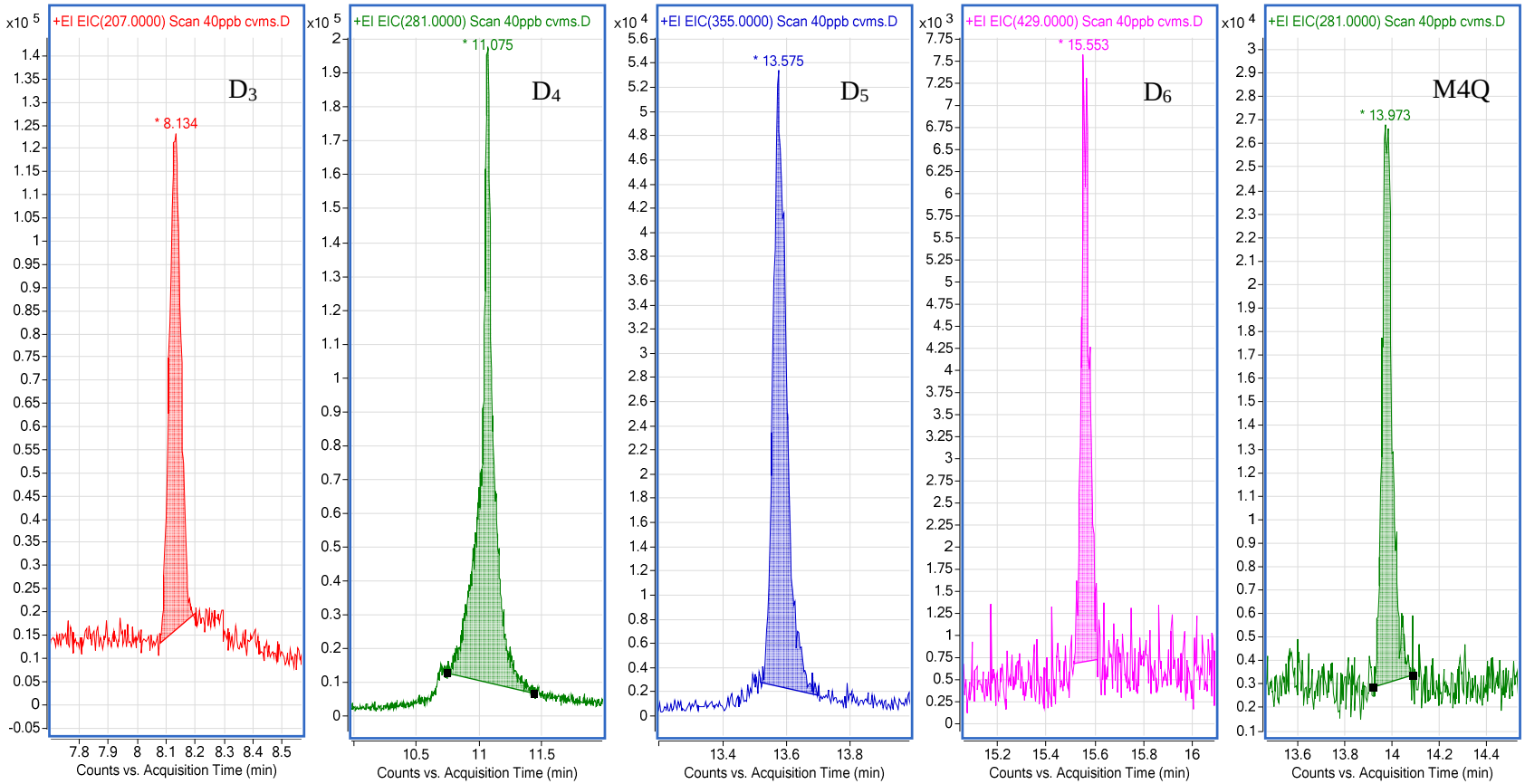


Figure 4-5. Extracted ion chromatographs of D_3, D_4, D_5, D_6 and M4Q for the analyses carried out in York.

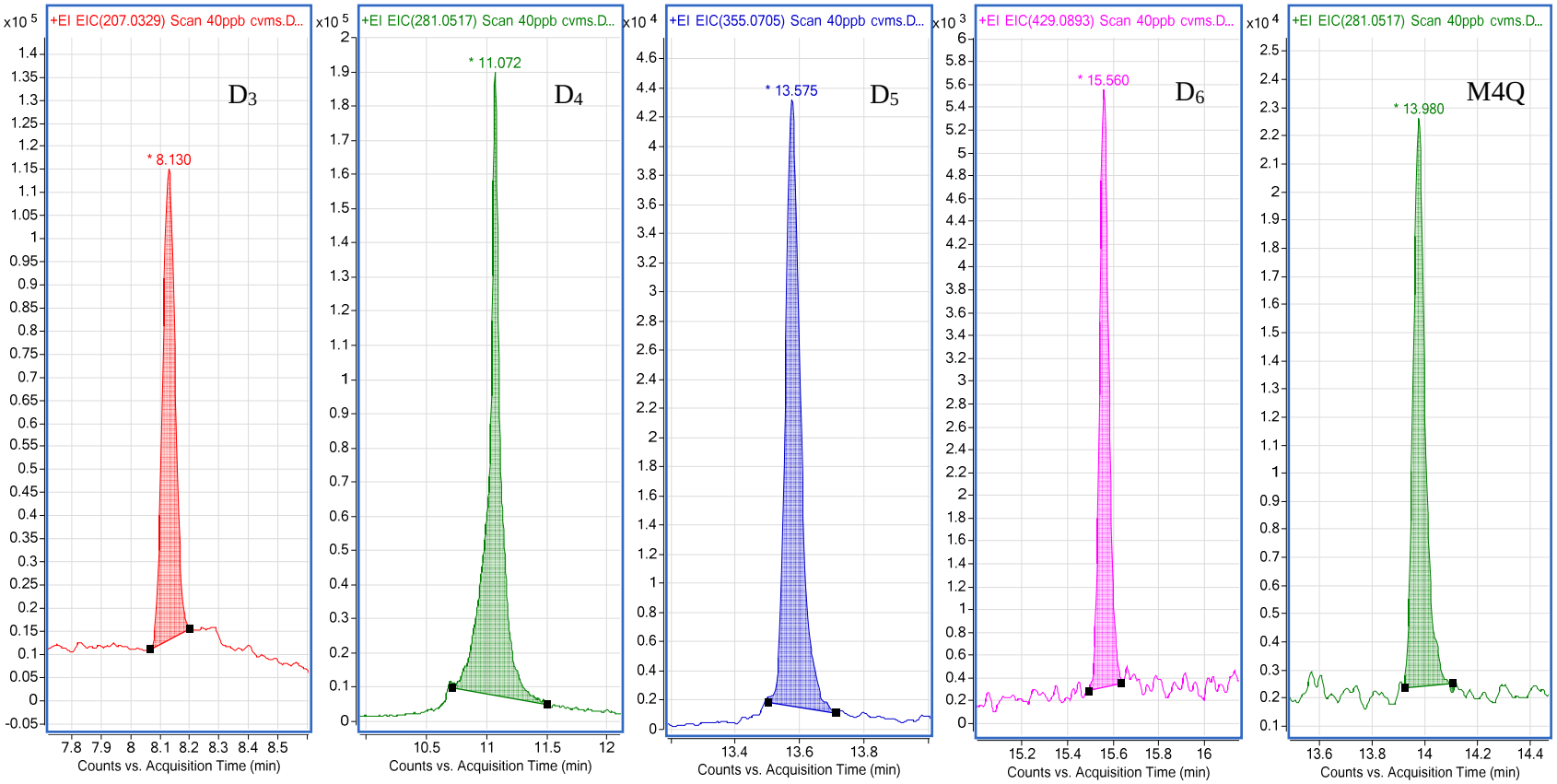


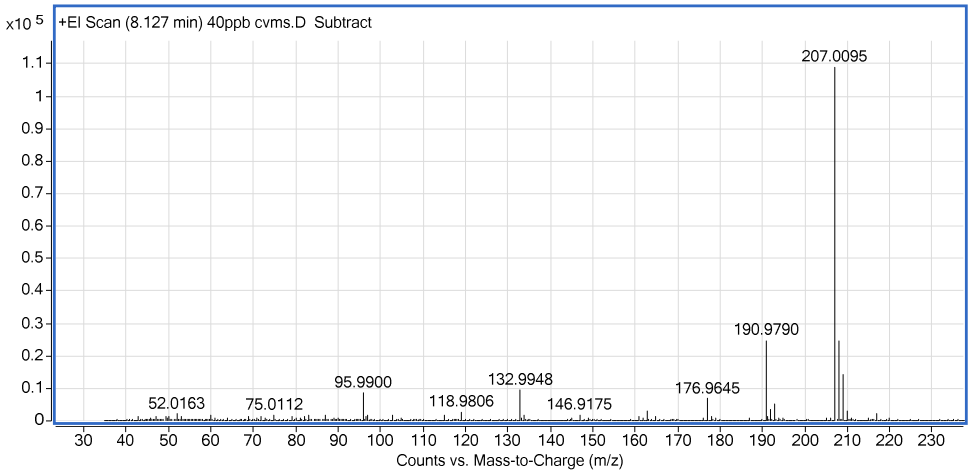
Figure 4-6. Extracted ion chromatographs of D_3, D_4, D_5, D_6 and M4Q at exact masses for the analyses carried out in York.

Table 4.2. Exact mass extracted ion analysis of cVMS and internal standard M4Q with TOF/MS.

Compounds	Extracted ion (m/z)	Extracted ion formula	Theoretical exact mass (M_t)	Empirical exact mass (M_e)*	Difference $\lvert M_t - M_e \rvert$	Mass error $\lvert M_t - M_e \rvert / M_t * 10^6$ (ppm)
Hexamethylcyclotrisiloxane, D_3	207	$C_5H_{15}O_3Si_3^+$	207.0329	207.0095	0.0234	113
Octamethylcyclotetrasiloxane, D_4	281	$C_7H_{21}O_4Si_4^+$	281.0517	281.0250	0.0267	95
Decamethylcyclopentasiloxane, D_5	355	$C_9H_{27}O_5Si_5^+$	355.0705	355.0415	0.029	82
Dodecamethylcyclohexasiloxane, D_6	429	$C_{11}H_{33}O_6Si_6^+$	429.0893	429.0568	0.0325	76
Tetrakis(trimethylsiloxy)silane, M4Q	281	$C_7H_{21}O_4Si_4^+$	281.0517	281.0247	0.027	96

*Empirical exact mass based on analysis of 40 ppb standard.

(a)



(b)

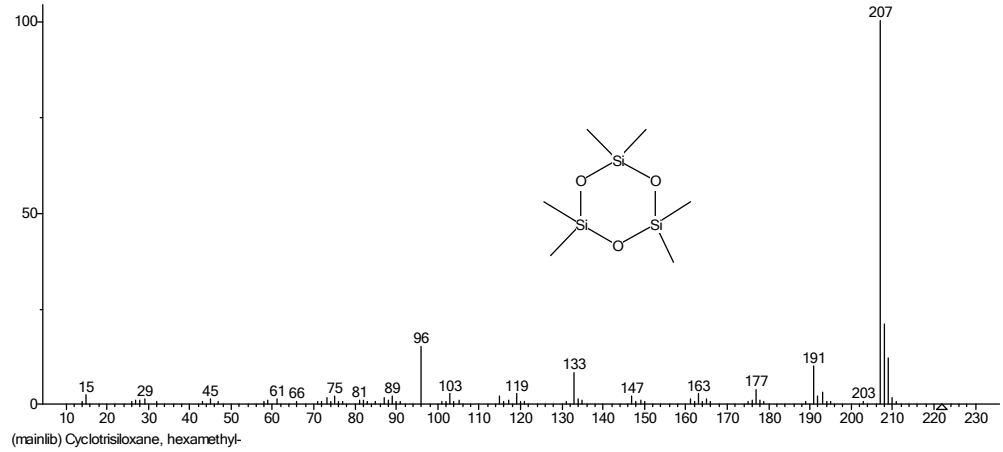
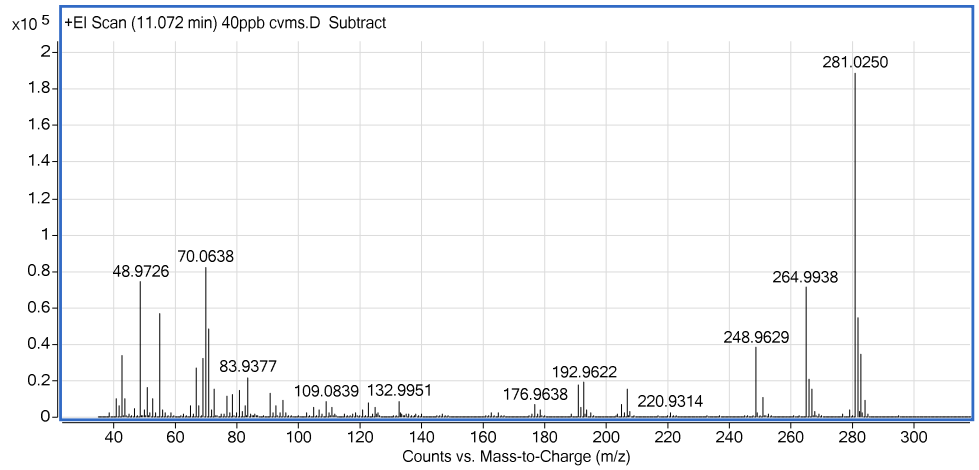


Figure 4-7. Mass spectra of D_3 (a) from 40 ppb standard and (b) from NIST MS library.

(a)



(b)

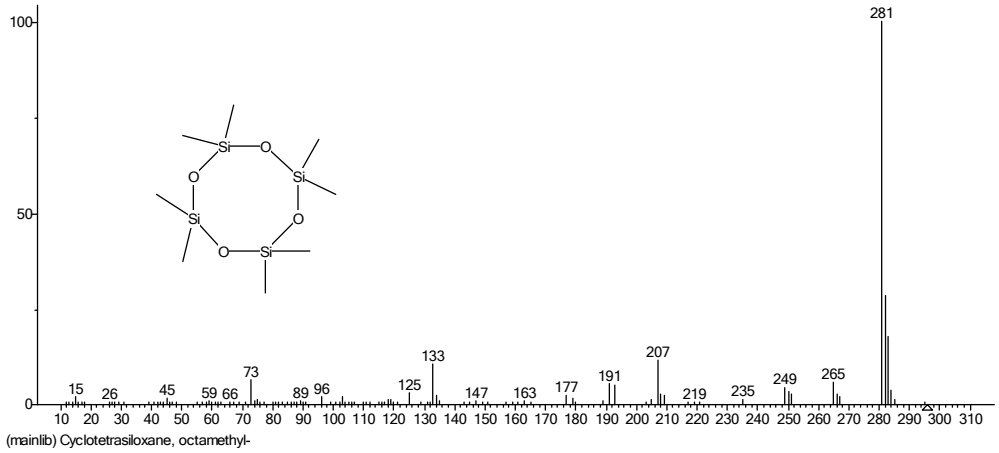
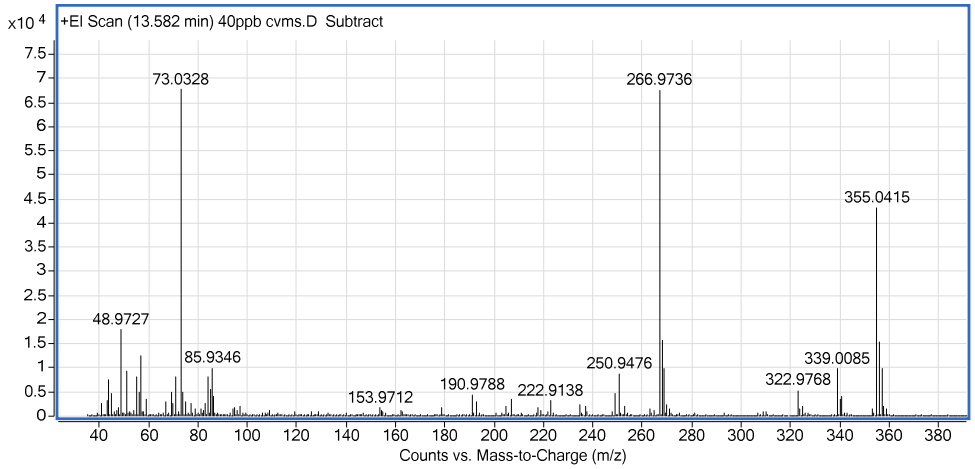


Figure 4-8. Mass spectra of D_4 (a) from 40 ppb standard and (b) from NIST MS library.

(a)



(b)

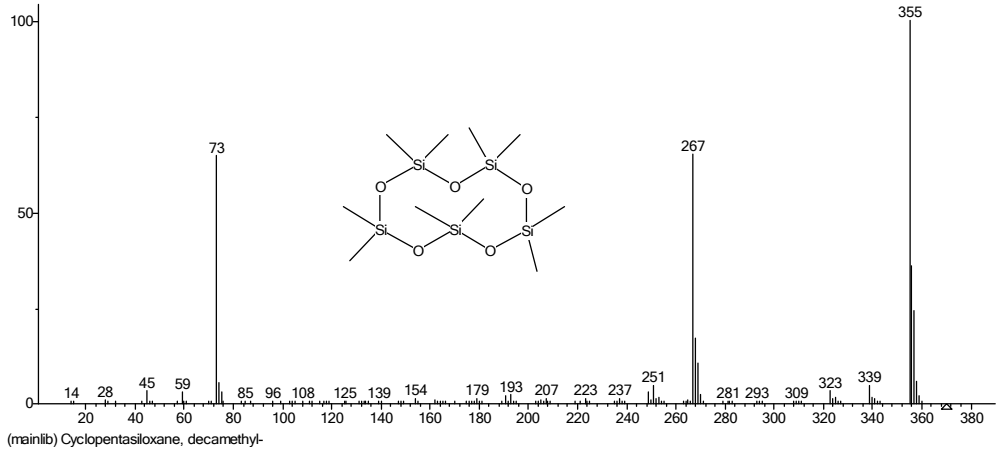


Figure 4-9. Mass spectra of D_5 (a) from 40 ppb standard and (b) from NIST MS library.

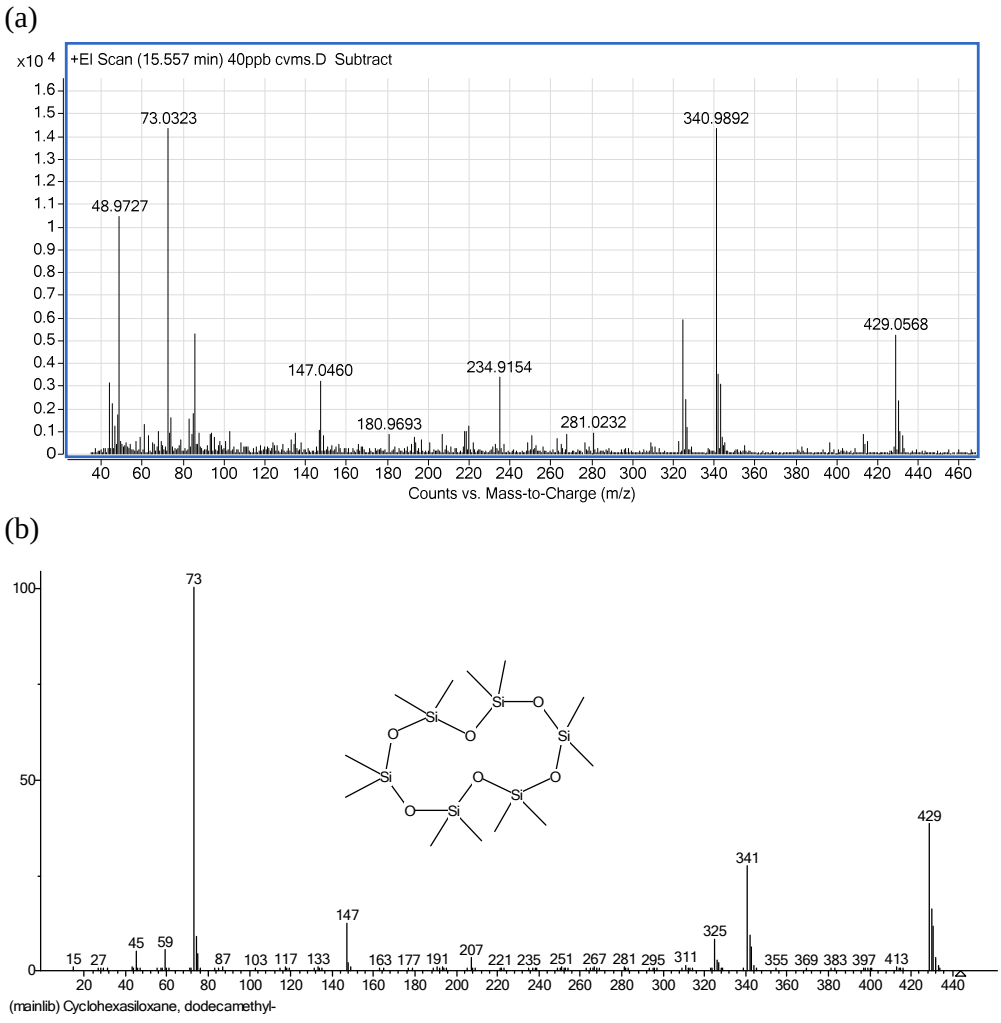


Figure 4-10. Mass spectra of D_6 (a) from 40 ppb standard and (b) from NIST MS library.

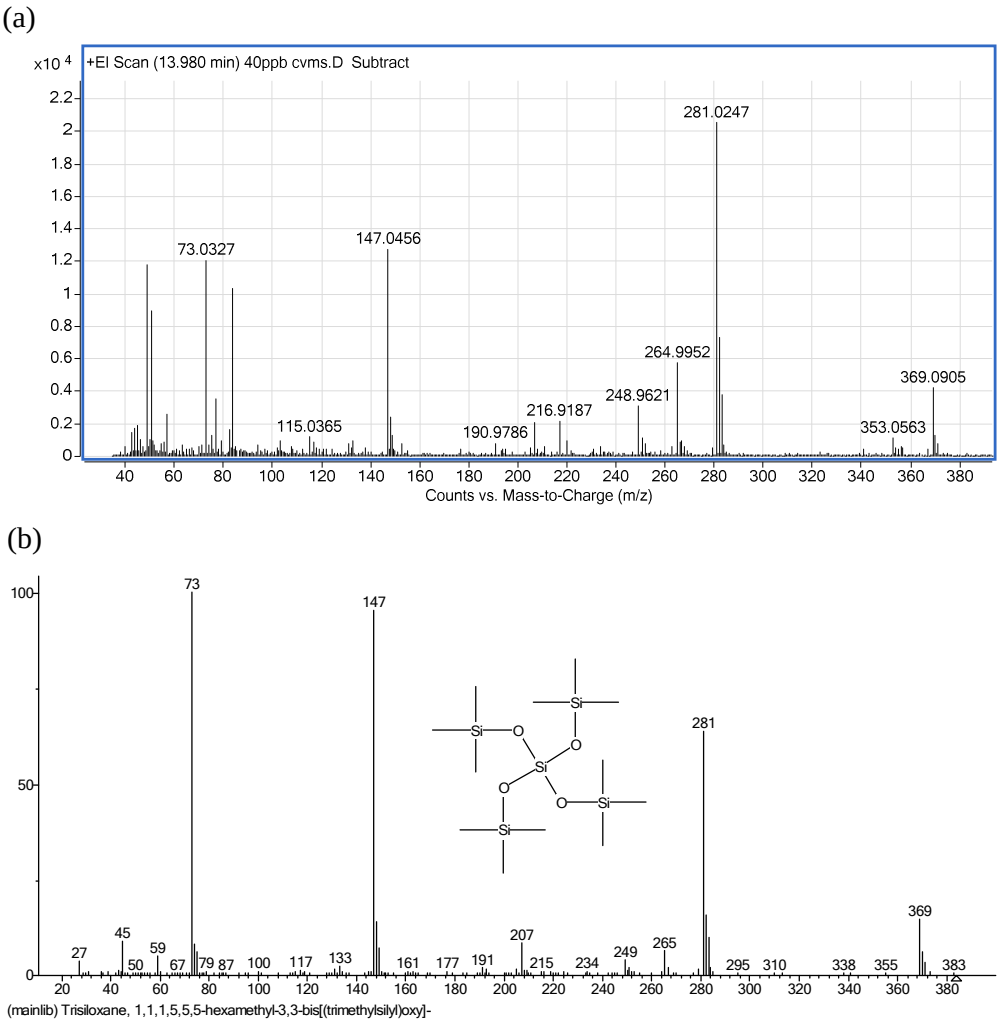


Figure 4-11. Mass spectra of M4Q (a) from 40 ppb standard and (b) from NIST MS library.

4.5 Sorbents and cartridges for cVMS analysis

Two different types of sorbents, ENV+ and ABN, were prepared to be packed into 1 mL cartridges prior to active sampling with pumps. Empty 1 mL cartridges (ISOLUTE Empty Reservoirs) and the respective frits were purchased from Biotage (Figure 4-12).

Figure 4-12. Cartridges and frits from Biotage.

The ENV+ sorbent was washed with hexane and dried with filtered N_2 (Figure 4-13).

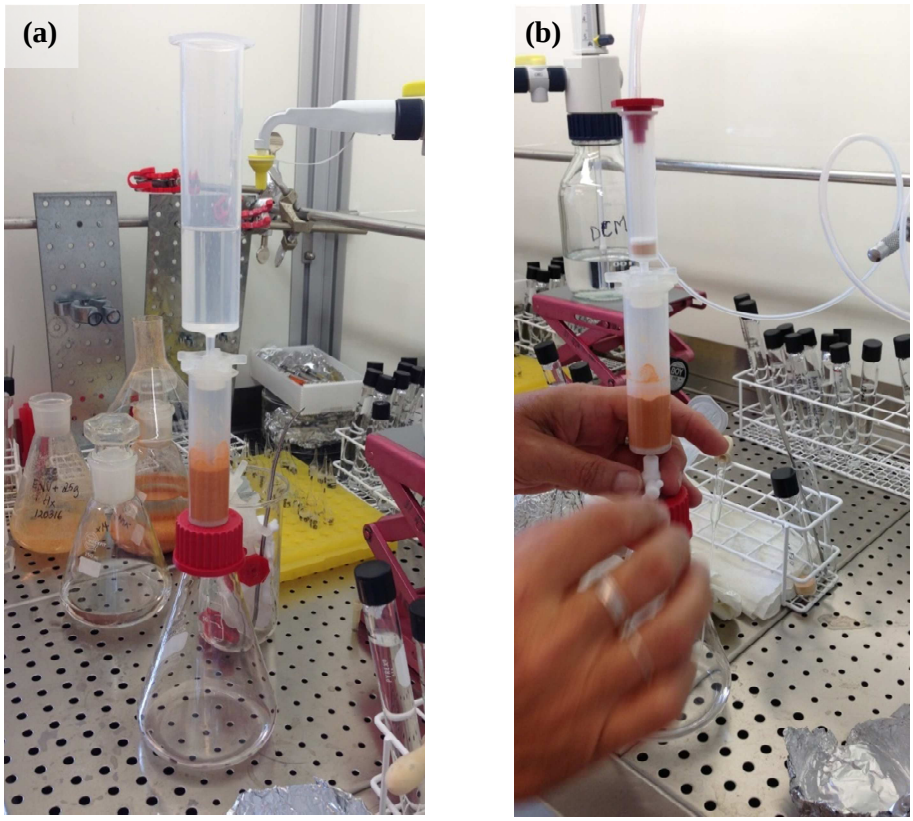


Figure 4-13. (a) ENV+ sorbent washed by hexane. (b) ENV+ sorbent dried with filtered N_2.

Dried ENV+ sorbent (10 – 15 mg) was weighed into a 1 mL cartridge and another frit was placed on top (Figure 4-14).

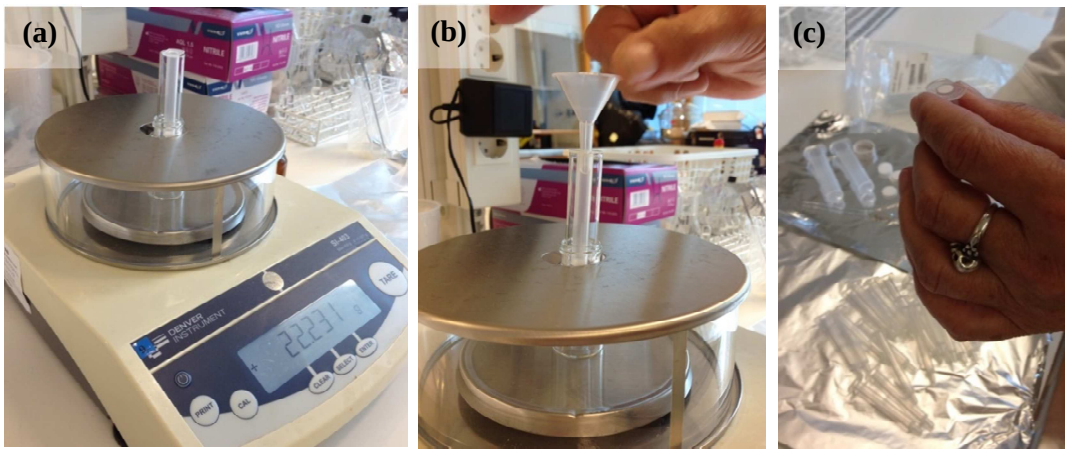


Figure 4-14. (a) & (b) Weighing of ENV+ sorbent into cartridges. (c) Top frit placed into cartridge, to be pushed in with a glass pipette.

Figure 4-15. A ready 1 mL cartridge filled with 10 – 15 mg of ENV+ sorbent.

The preparation of ABN sorbent is different from ENV+ sorbent because it is difficult to handle when dried. It was added wet (in hexane) to 1 mL cartridges directly to about the height of the prepared ENV+ cartridges. A frit was then added on top, before filtered N_2 was connected to dry it (Figure 4-16).

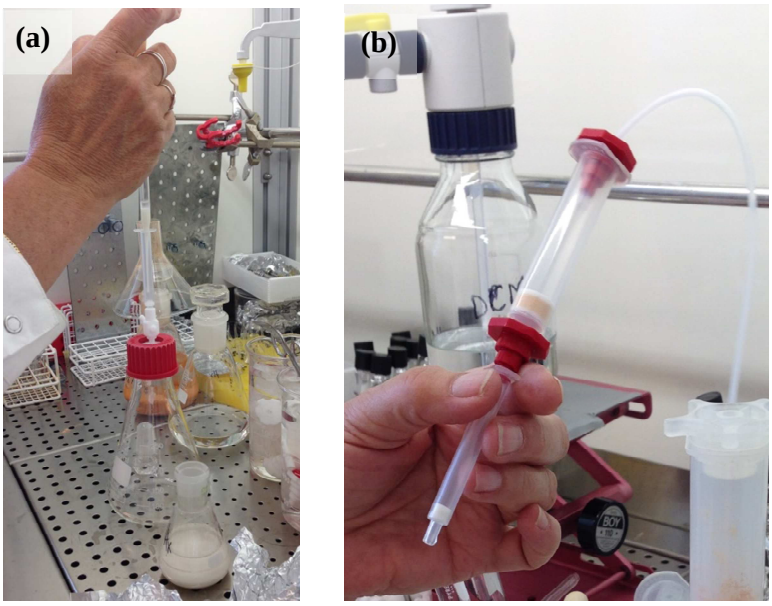


Figure 4-16. (a) Wet ABN added directly into 1 mL cartridges. (b) ABN dried with filtered N_2.

The remaining washed and dried ENV+ sorbent was kept in a 20 mL cartridge with cap and lid. The filled cartridges were kept wrapped in aluminium foil, in a sealed bag.

Before the filled cartridges were used for sampling, they were washed with 5 mL of hexane followed by 5 mL of DCM.

4.6 Active sampling

Before the filled 1 mL cartridges were used for sampling, they were washed with 5 mL hexane, followed by 5 mL DCM.

Active sampling was carried out in the laboratory. 1 ENV+ cartridge and 1 ABN cartridge were used as blanks and were placed on the bench top. Another ENV+ cartridge and ABN cartridge was connected to pumps. The volumetric reading on

the pumps was noted at the start of the sampling and at the end so the amount of air sampled can be calculated. The start and end time was also noted to record the duration of sampling. M4Q was used as the internal standard or volumetric standard. M4Q was diluted to about 2 ng μL^{-1}. During elution, 20 µL of M4Q was spiked onto the top of the frits for the 4 cartridges (1 ABN blank, 1 ENV+ blank, 1 ABN sample, 1 ENV+ sample).

After sampling overnight, cartridges were collected and immediately prepared for analysis. They were eluted with 0.6 mL of DCM into a GC vial. It was observed that ENV+ cartridges eluted faster. The GC vials were then covered with aluminium foil and then with a cap without the PTFE septum. A M4Q reference (20 uL of M4Q + 0.6 mL DCM) was prepared as well. All the prepared GC vials were then sent to the GC-MS for analysis.

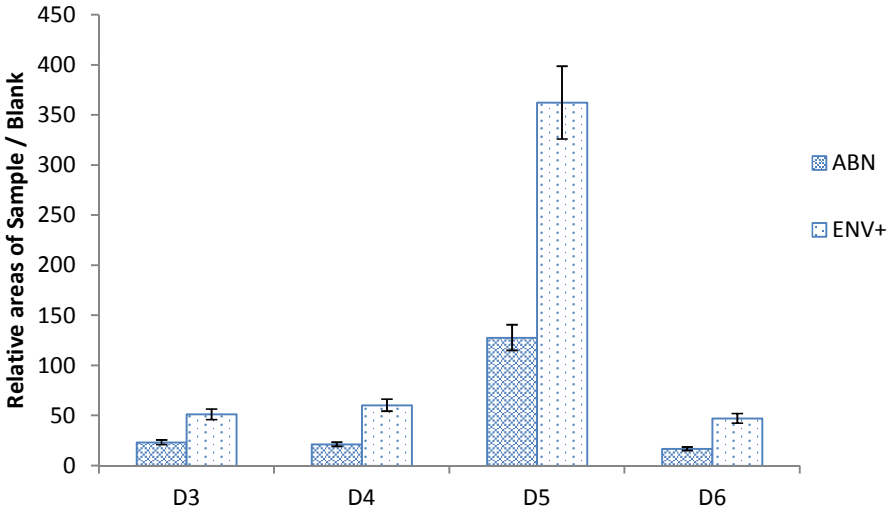


Figure 4-17. Ratios of the relative areas of the compounds to their respective blanks for active sampling using ABN and ENV+ sorbents.

The relative areas were calculated by dividing the respective GC peak areas of the compounds by the GC peak area of the M4Q internal standard. The ratios of the

relative areas of the compounds to the blanks were derived and plotted. From the results obtained (Figure 4-17), it seemed that ENV+ was the better sorbent of choice for the analysis of cVMS.

4.7 Passive sampling

Whilst active sampling has been shown to be successful, it is a less appropriate method to deploy in large numbers of homes, due to cost and the more intrusive nature of the sampler. This study investigates the role for passive sampling as a means to access a wider measurement base within domestic homes and in indoor environments more generally. Passive sampling is potentially more cost efficient, does not require electricity and is silent. It provides time-averaged sampling which in turn gives a reasonable averaged overview of the concentrations in a given indoor environment. This work reports the development of a passive sampling method for the measurement of cVMS levels in indoor air with good blank values and appropriate limits of detection for assessment in domestic settings. The passive sampling method was calibrated against active sampling running in parallel over the period of the exposure of the passive samplers. The active method was identical to the one used by Kierkegaard and McLachlan [162].

4.7.1 Passive sampling with sorbents in cartridges

It was proposed that passive sampling be carried out using cartridges without the top frit, thereby exposing the sorbents in the cartridges to open air. A larger cartridge was used for the passive sampling so as to have a larger exposed surface area. 30 mg of ENV+ sorbent was weighed and placed in 6 mL cartridges. ABN of about the same height was also pipetted into 6 mL cartridges. Another set of cartridges containing the different sorbents (1 ENV+ and 1 ABN) without the top frit was also prepared and used as blanks.

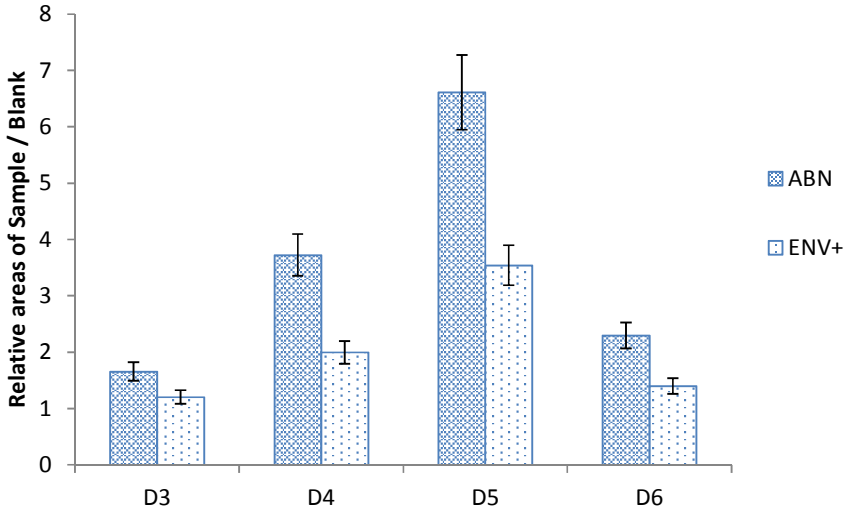


Figure 4-18. Ratios of the relative areas of the compounds to their respective blanks for passive sampling using exposed ABN and ENV+ sorbents.

It is observed that the sample relative areas are not significantly higher than that of their blanks (Figure 4-18). The ratios ranged from about 1.6 to 6.6 for ABN and 1.2 to 3.5 for ENV+. Another passive sampling method was therefore explored.

4.7.2 Passive sampling using sorbents packed in bags

It was proposed that sorbents be packed in polyamide (PA 6.6 Monofilament Yarns, Monosuisse AG) bags as means for passive sampling. Pieces of nylon were cut out and heat-sealed to create a bag to hold the sorbents. The pore size of the bags (about 50 μm) were too big for ABN sorbents, hence only ENV+ sorbents were tested for this passive sampling method.

2 nylons bags were filled with 30 mg of ENV+ sorbent and hooked onto a paper clip. These bags were then hung on a cupboard in the laboratory overnight. Additionally, 2 blanks were prepared: 1 blank consisted of an empty nylon bag in

a sealed tube, and the other blank consisted of a nylon bag with 30 mg of ENV+ sorbent in a sealed tube.

After about 16 hours of sampling (overnight), the nylon bags were collected and immediately prepared for analysis. They were placed in tubes and sealed with aluminium foil and a cap. It was shaken manually with DCM for about 1 minute. The DCM extract was then pipetted out into a GC vial and 30 uL of M4Q was added. The samples were sent to the GC-MS for analysis.

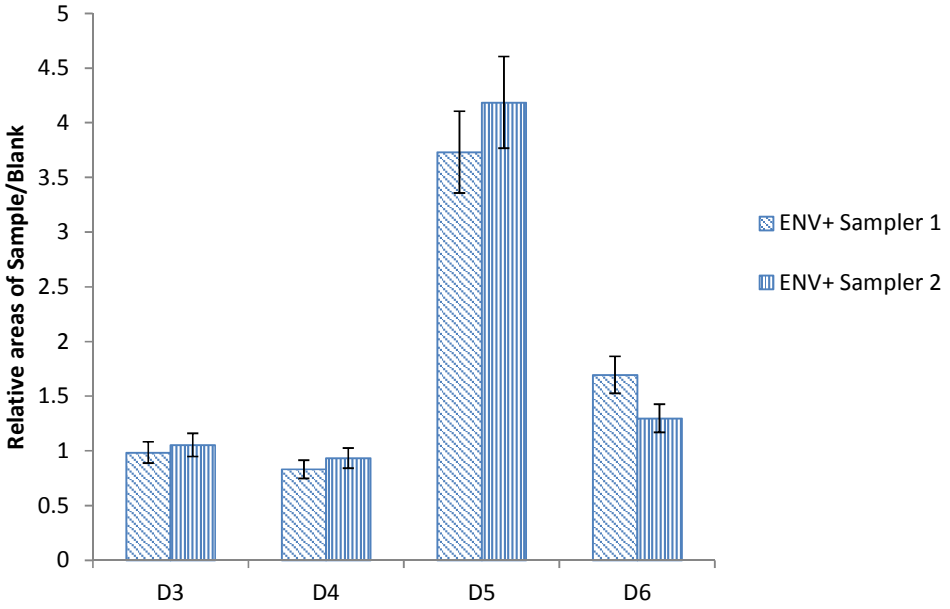


Figure 4-19. Ratios of the relative areas of the compounds to their respective blanks for ENV+ sorbents in passive sampling bags.

From the results obtained (Figure 4-19), it was observed that the sampling process was somewhat repeatable with good agreement of the two passively sampled bags. However from the areas of the peaks from the chromatograph, it was observed that blank ENV+ had high levels of cVMS. There may be some contamination in the ENV+ sorbents, and hence resulting in the low ratios observed.

4.7.3 Cleaning of passive sampling bags

The nylon bags were soaked in DCM and sonicated. After sonication, they were dried with filtered N_2. One of these cleaned bags was put into a vial and shaken manually with 1 mL of DCM for 1 minute. The DCM extract was pipetted out into a GC vial and sent for analysis.

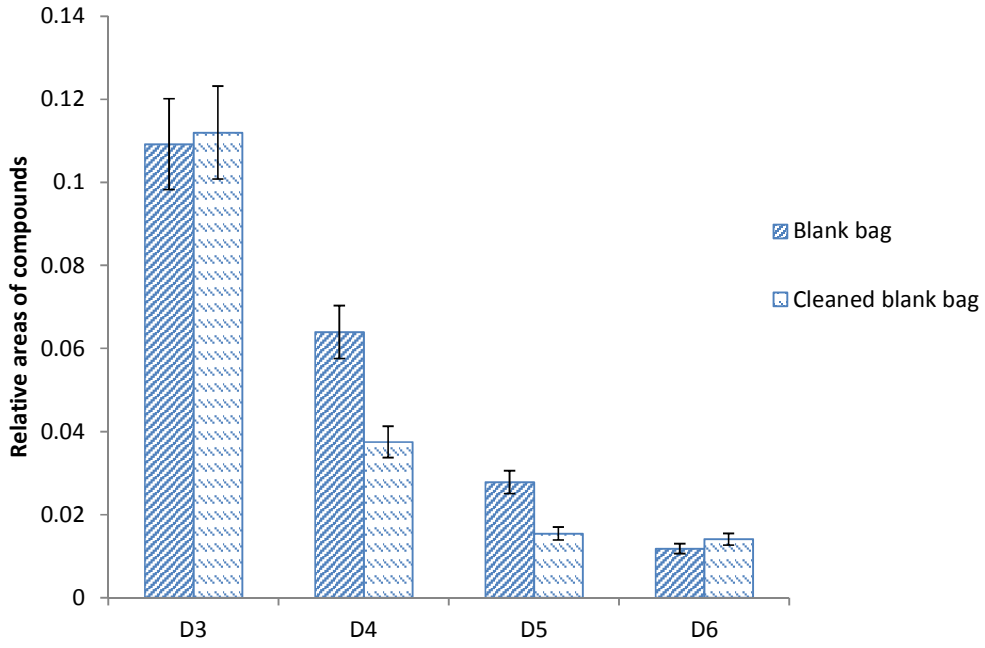


Figure 4-20. Comparison of cVMS levels in passive sampling bags before and after cleaning.

As seen from Figure 4-20, the levels of D_4 and D_5 were significantly lower after washing, thus it was noted that the bags should be washed before sampling.

4.7.4 Positioning of sampling bags

Similar to the preparation before, 2 nylon bags were filled with 30 mg of ENV+ and hooked on a paper clip. One of the bags was hooked on the cupboard, while

the other was placed on the fumehood sash such that it received some “draft” due to the airflow into the fumehood. Additionally, 2 blanks were prepared: 1 blank consisted of an empty nylon bag in a sealed tube, and the other blank consisted of a nylon bag with 30 mg of ENV+ sorbent in a sealed tube.

After about 16 hours of sampling (overnight), the nylon bags were collected and immediately prepared for analysis. They were placed in tubes with DCM and sealed with aluminium foil and a cap. It was sonicated at 25 °C for 5 minutes. 30 µL of M4Q was added to each tube and the tubes were vortexed. The DCM + M4Q extract was then pipetted out into a GC vial. The samples were analysed by GC-MS.

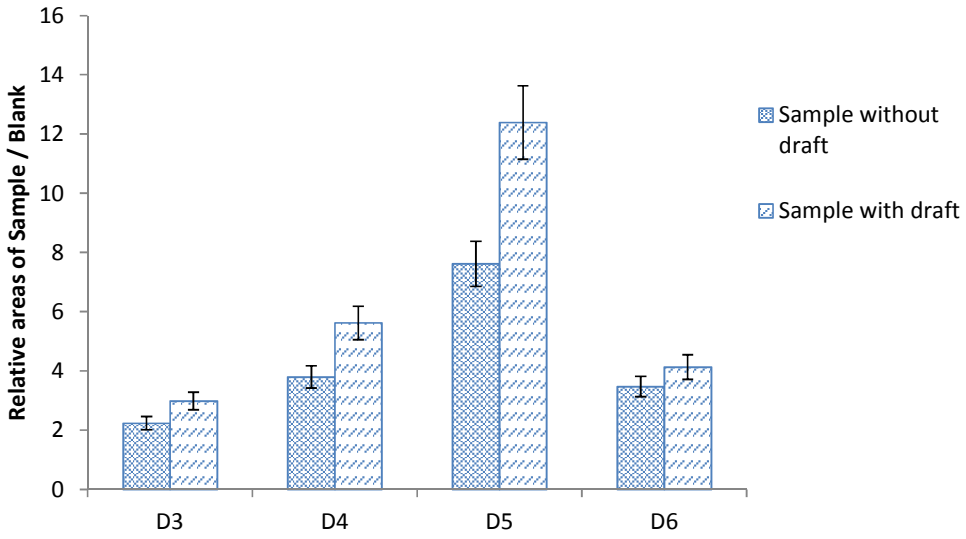


Figure 4-21. Ratios of the relative areas of the compounds to their respective blanks for passive sampling bags placed in still and drafty locations.

It was observed that some air movement might increase the efficiency of a passive sampling method (Figure 4-21).

4.7.5 Exploring different packaging of passive samplers

Various tests with different passive sampling bag designs were carried out to find the most efficient bag design. Tests were carried out with bags loosely packed and tightly packed with ENV+ sorbent.

The bags were threaded with a string before they are placed on a hook. This allowed the bags to move more freely and move around more. It was hoped that an increase in the movement of the bags would result in a better sampling efficiency.

3 bags were prepared as in previous samplings. The first bag was about 2 x 2 cm in size. One bag was made slimmer about 2 x 1 cm and filled with 30 mg ENV+ sorbent. Another bag was made even thinner about 2 x 0.5 cm and filled with 20 mg ENV+ sorbent (see Figure 4-22).

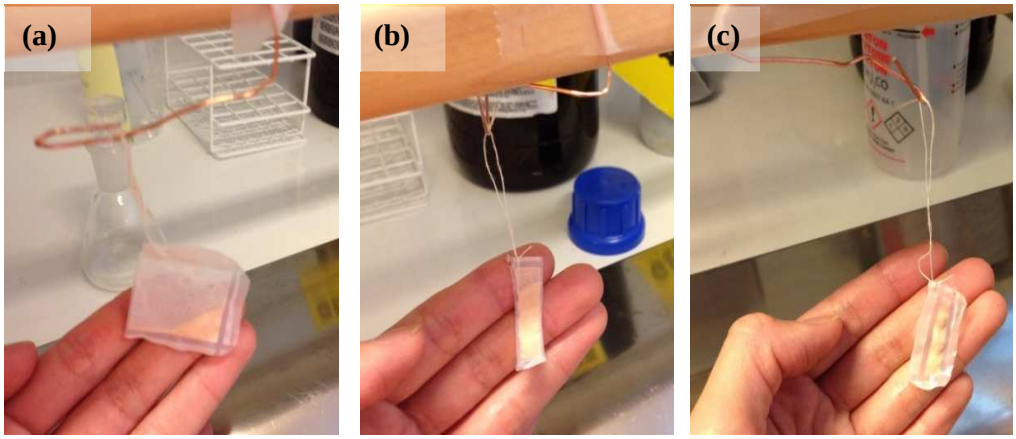


Figure 4-22. (a) Nylon bags with 30 mg ENV+ sorbent prepared. (b) Slimmer bags with 30 mg ENV+ sorbent. (c) Even thinner bags with 20 mg ENV+ sorbent.

2 blanks were prepared: 1 blank consisted of an empty nylon bag in a sealed tube, and the other blank consisted of a nylon bag with 30 mg of ENV+ sorbent in a sealed tube.

After about 16 hours of sampling (overnight), the nylon bags were collected and immediately prepared for analysis. They were placed in tubes with DCM and sealed with aluminium foil and a cap. It was sonicated at 25 °C for 5 minutes. 30 µL of M4Q was added to each tube and the tubes were vortexed. The DCM + M4Q extract was then pipetted out into a GC vial. The samples were sent to the GC-MS for analysis.

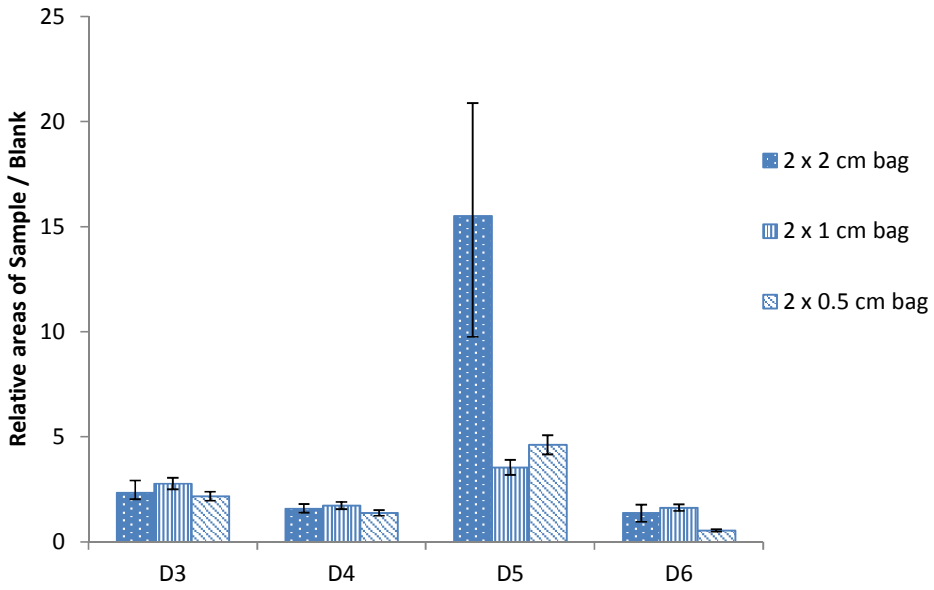


Figure 4-23. Ratios of the relative areas of the compounds to their respective blanks for passive sampling bags of different sizes.

From Figure 4-23, it was observed that bag designs that were tightly packed with sorbent resulted in a lower absorption efficiency compared to the loosely packed. It could be inferred that this may be due to the slower rate of transfer of compounds from the exposed sorbent on the surface of the bag to the unexposed sorbents inside the bag. Further tests were to be carried out on the designs of the bags.

In the next set of samples, the bags were made of a slimmer design but with some space so that ENV+ sorbents were still loosely packed (see Figure 4-24). In order to increase the surface area of sorbents exposed and whilst keeping the sorbents loosely packed, compartmentalised bags were made. Nylon bags with 3 compartments were filled with 10 mg of ENV+ sorbent in each component, giving a total mass of 30 mg for each passive sampler. The efficiency of this design was compared to a non-compartmentalised bag containing 30 mg of ENV+ sorbent.

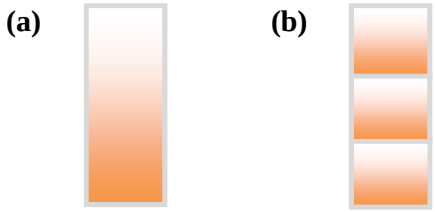


Figure 4-24. (a) Non-compartmentalised sampling bags design.
(b) Compartmentalised passive sampling bags design to spread out sorbents in bag.

After about 16 hours of sampling in the shower room (overnight), the nylon bags were collected and immediately prepared for analysis. They were placed in tubes with DCM and sealed with aluminium foil and a cap. It was sonicated at 25 °C for 5 minutes. 30 µL of M4Q was added to each tube and the tubes were vortexed. The DCM + M4Q extract was then pipetted out into a GC vial. The samples were sent to the GC-MS for analysis.

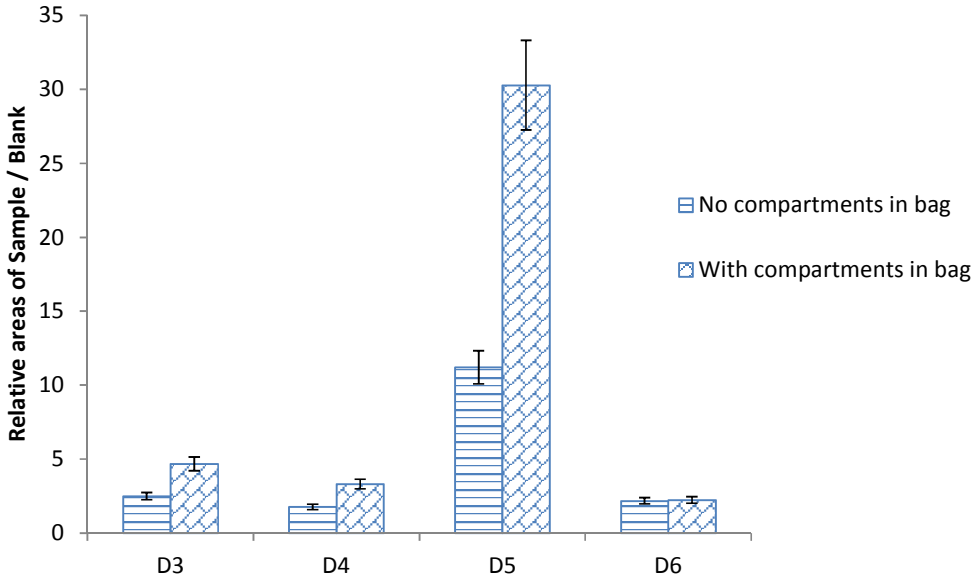


Figure 4-25. Ratios of the relative areas of the compounds to their respective blanks for non-compartmentalised and compartmentalised passive sampling bags.

The results showed that compartmentalising the bags increased the efficiency of the sampling process (Figure 4-25). As opposed to a tightly packed bag as seen previously, a loosely packed bag seemed to allow for a better sampling efficiency.

Tests were carried out to test if having more compartments (Figure 4-26 and Figure 4-27) would increase the sampling efficiency.

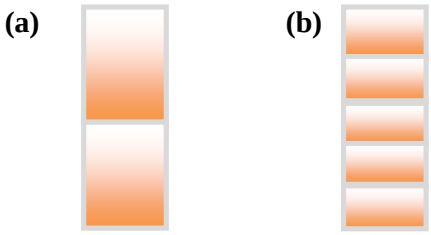


Figure 4-26. (a) Compartmentalised passive sampling bags design. (b) More compartmentalised passive sampling bags design.

Figure 4-27. Bags with different number of compartments, both containing 30 mg of ENV+ sorbent each.

After about 64 hours of sampling in the shower room (over the weekend), the nylon bags were collected and immediately prepared for analysis. They were placed in tubes with DCM and sealed with aluminium foil and a cap. It was sonicated at 25 °C for 5 minutes. 30 µL of M4Q was added to each tube and the tubes were vortexed. The DCM + M4Q extract was then pipetted out into a GC vial. The samples were sent to the GC-MS for analysis.

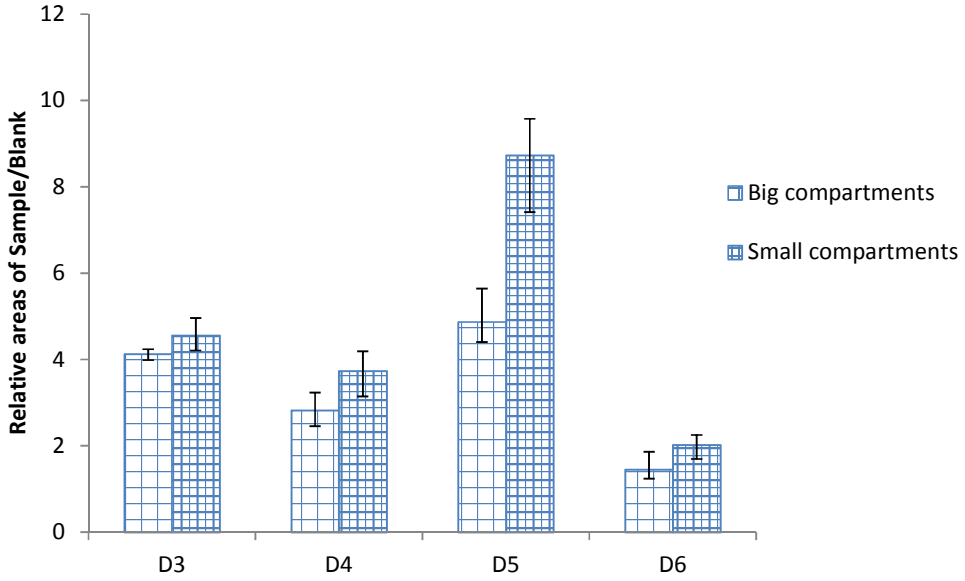


Figure 4-28. Ratios of the relative areas of the compounds to their respective blanks for passive sampling bags with big and small compartments.

As seen from Figure 4-28, having smaller compartments seemed to better the efficiency of the sorbent. It was decided that the final design used for calibration with active sampling in the next set of experiments would have 3 compartments (a balance between having good efficiency and ease of preparing the bags).

For the passive sampling suited to our purposes, an accumulative passive sampling method would be preferred to obtain a good average of the levels of cVMS in indoor environments. Factors affecting an accumulative passive sampler would be turbulence (i.e. wind or draft), surface area of the sorbent exposed, mass of sorbent used and time. The design of the passive samplers took into account these factors to best suit our purpose and aim for indoor sampling over a period of, for instance, a week. By putting the sorbents into a nylon bag, it lowered the impact of turbulence on the sampling process as any draft in the vicinity of the bags would not be directly in contact with the sorbents; there is a “cushioning

effect" from the layer of nylon holding the sorbents. The separation of the bags into different components helped to spread out the sorbents without causing it to be too packed together, allowing for an increase in surface area. The mass of sorbents used was kept constant and was estimated to be sufficient to allow a linear calibration curve when calibrated against active sampling over a period of 10 days.

4.8 Calibration of passive sampling method

Chemicals are taken up in a passive sampler by diffusion from ambient air to the passive sampling medium. This process follows the model as shown in Figure 4-29 [170].

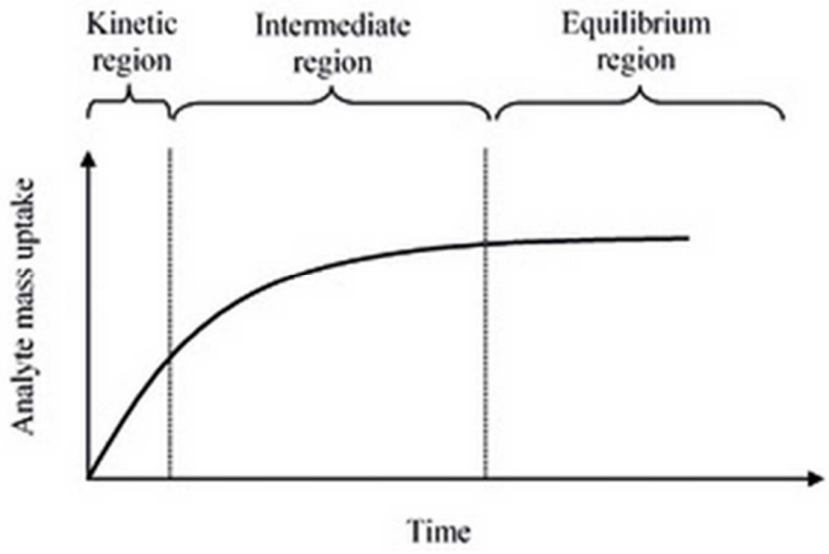


Figure 4-29. Passive sampling model.

A calibration study is necessary to be able to calculate the concentrations in air based on the amount of a chemical that is observed using this passive sampling method. There are three difference phases in the passive sampling model. When the passive sampler is first placed in the sampling medium, there is a linear

accumulation phase. This will be followed by a non-linear increase and finally reaching equilibrium, defined by the partition coefficient of the analyte [78, 170]. With the calibration study, the duration of the linear phase and the passive sampling rate within this phase can be determined.

Passive sampling bags were prepared. Nylons bags with 3 compartments were filled with 10 mg of ENV+ in each component, giving a total mass of 30 mg for each passive sampler. A seven-point calibration was to be carried out, hence seven sets of passive samplers, consisting of 1 blank and 2 samplers in each set, were prepared. Blanks were placed in tubes covered with aluminium foil and capped.

The passive samplers were calibrated against active sampling using ENV+ in 1 mL cartridges, using the method established by Kierkegaard and McLachlan [162]. Seven sets of passive samplers, consisting of 1 blank and 2 samplers in each set, were prepared. Blanks were placed in tubes covered with aluminium foil and capped. Similarly, seven sets of active samplers (15 mg ENV+ cartridges), consisting of 1 blank and 2 samplers in each set, were prepared. Before the cartridges were used, they were washed with 5 mL hexane followed by 5 mL DCM. Blanks were capped on both ends of the cartridges and wrapped in aluminium foil.

At the start of the sampling, all the passive samplers were threaded on a string and hung on a paper clip, and all the blanks for the passive samplers were kept in sealed tubes near the passive samplers (Figure 4-30). The blanks of the active sampling were attached to the pump for a few seconds before they were capped and wrapped in foil (Figure 4-31a). Two ENV+ cartridges were used in parallel for duplicate sampling (Figure 4-31b). The active sampling set up is shown in Figure 4-32.

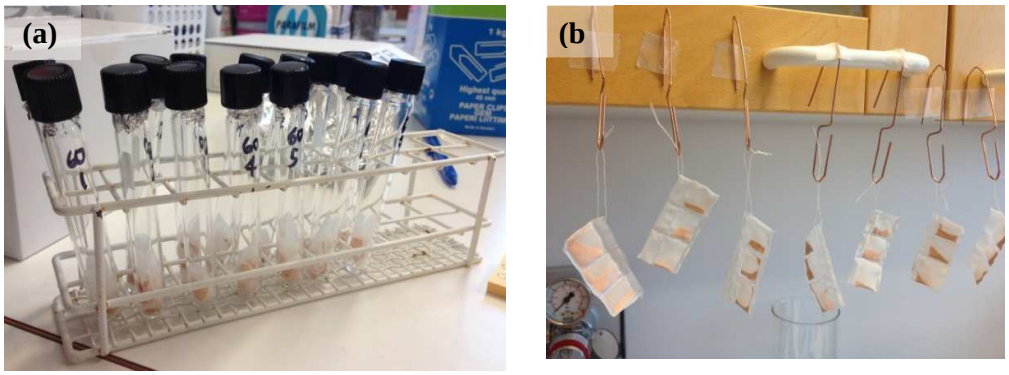


Figure 4-30. (a) Blanks for passive sampling. (b) Passive samplers hung on a paper clip.

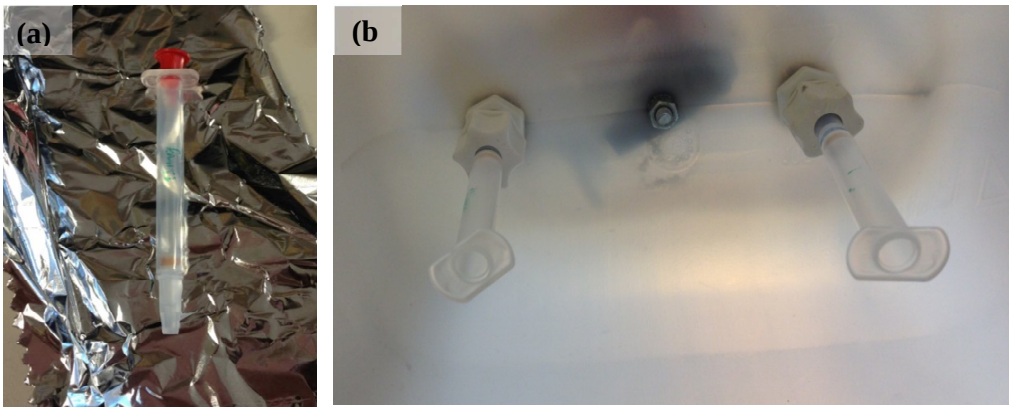


Figure 4-31. (a) Capped cartridge as blank for active sampling. (b) Two cartridges attached to pumps in parallel for active sampling.

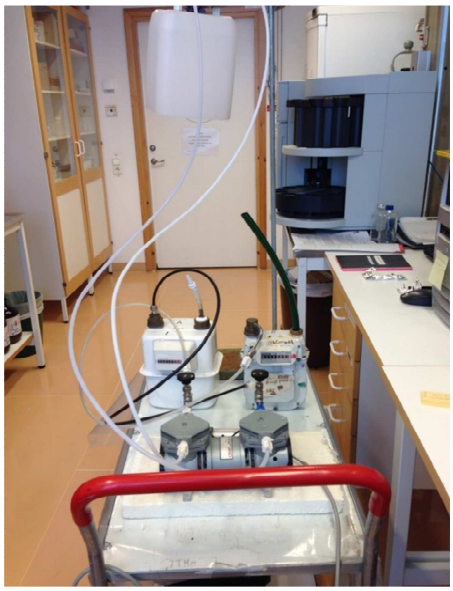


Figure 4-32. Active sampling set-up with pumps and volumetric flow meter.

At the end of each sampling period, the passive samplers were collected and immediately prepared for analysis. They were placed into a tube and sonicated with 1 mL of DCM at 25 °C for 5 minutes. 30 µL of M4Q was then added to each of the tubes before the extract was pipetted out into GC vials. The active samplers were eluted with 1 mL DCM, and 30 µL of M4Q was added post-elution. Before GC-MS analysis the extract from the active samplers were diluted with another 1 mL or 2 mL of DCM as appropriate.

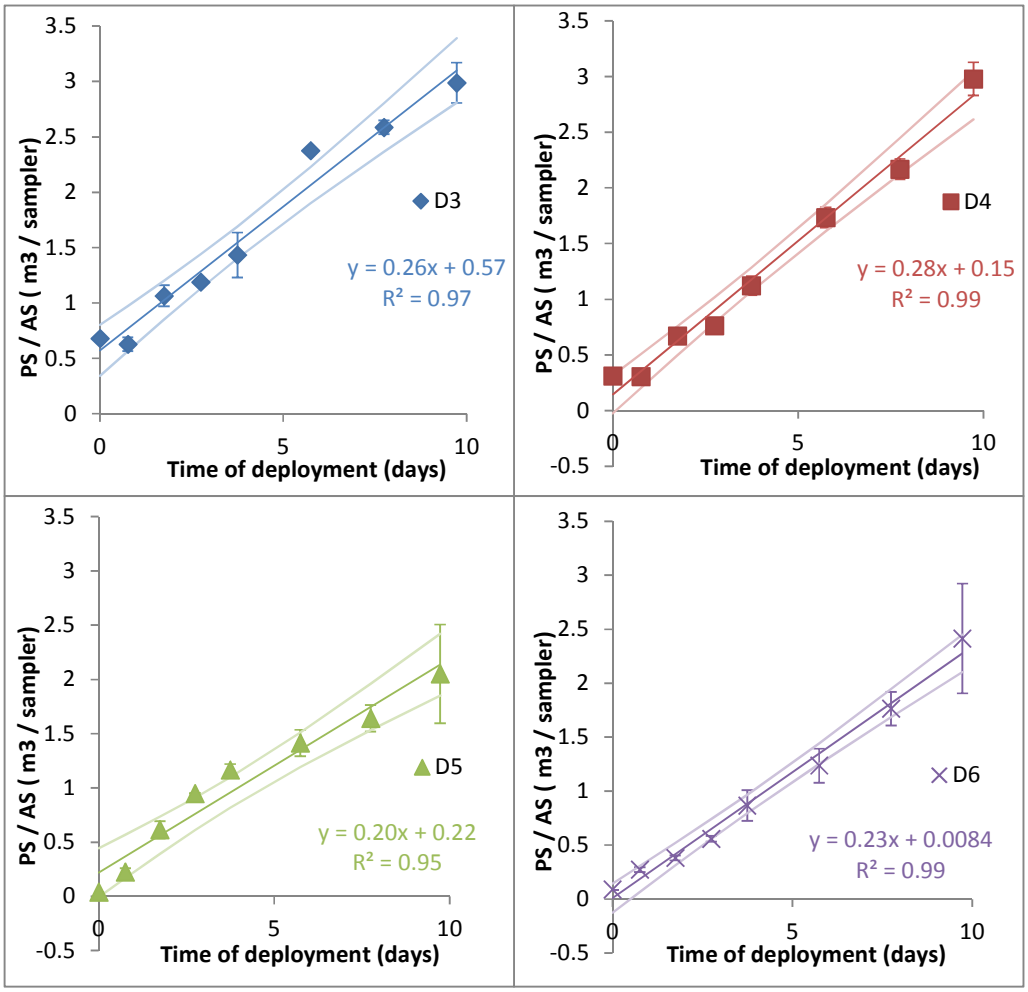


Figure 4-33. Analyte cVMS collected as a function of passive sampler deployment time.

Calibration curves were plotted as the relative peak areas of the analytes in the passive sampler divided by the relative areas per m^3 of the respective analytes in air (active sampler) against the time of deployment (Figure 4-33). Results for blank samples extracted at the start of the experiment divided by the average concentration in air for the whole period was included in the calibration plot at time zero.

Based on the results from the calibration curves, the uptakes for the cVMS were considered to be relatively linear throughout the sampling period of about 10 days. The passive sampling rate as seen from the slopes of these curve ranged from 0.20 to 0.28 m^3 of air per sampler per day. After 10 days of deployment, none of the cVMS had reached equilibrium with the passive sampler.

4.9 Storage of passive samplers in glass vials

In the transport of the passive samplers to the sampling location and their return to the laboratory to be analysed, these samplers have to be kept sealed to prevent contamination. One idea was to keep the sampler in a glass jar, attached to the cap via a string, such that it would be easy to handle without touching it before and after sampling (Figure 4-34).

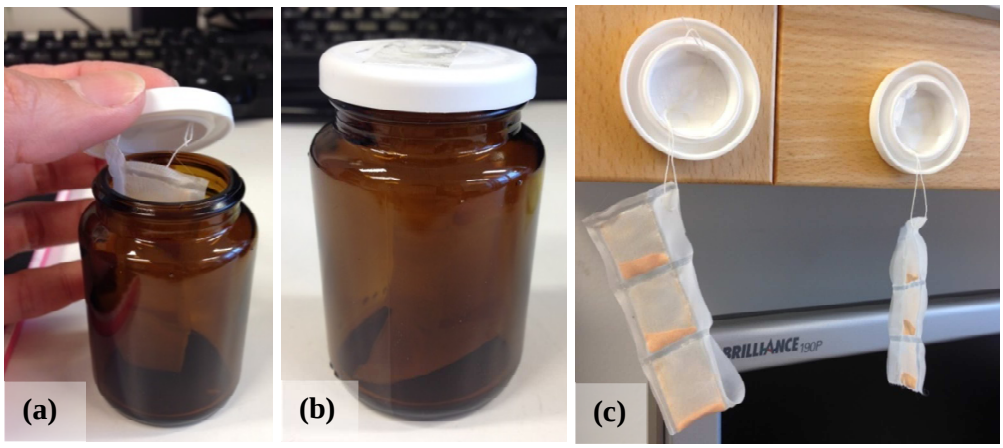


Figure 4-34. (a) Vial with passive sampler attached to the cap with a string and tape. (b) Closed vial during storage and/or transport. (c) Passive samplers attached to the cap of the vial. Vial cap has an adhesive so it can be stuck onto any surface for sampling.

Six passive samplers were prepared and sampled over 2 days. One was analysed immediately while the other five were stored in the vial for 1, 2, 3, 4 and 7 days respectively before they were analysed.

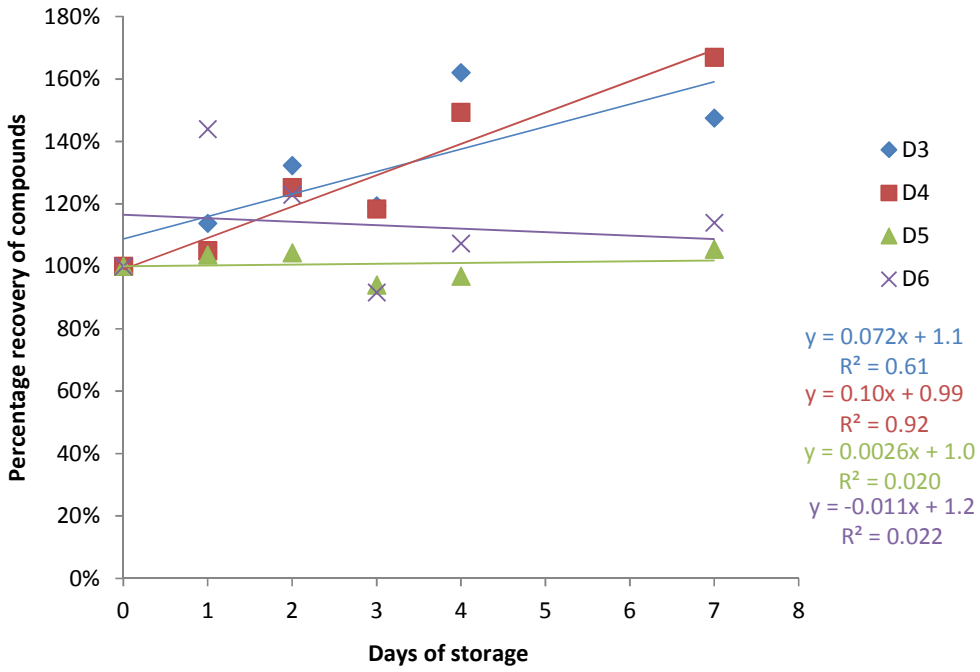


Figure 4-35. Percentage recovery of cVMS over the storage period.

As seen from Figure 4-35, the storage experiments show only small changes in the concentrations of D_5 and D_6 with increased storage time in the glass vials. However, concentrations of D_3 and D_4 increased at an average rate of 7 % and 10 % per day respectively. At the 95 % confidence level, the storage experiment showed no significant change in levels of D_3 ($p = 0.067$), D_5 ($p = 0.79$) and D_6 ($p = 0.78$). Earlier studies have shown that D_5 may degrade to D_4 and D_3 on the ENV+ resin in cartridges when stored at -18 °C [171]. However in this storage experiment, the increase in D_4 and D_3 did not correlate to any decreases in D_5. In addition, the amount of D_5 present was calculated to be only about 4 times more

than D_4. If the 10 % gain in D_4 was due to degradation from D_5, the percentage decrease in D_5 levels should be at least 2 % which was not the case in this study.

4.10 Blank levels and LOD values

The limits of detection (LOD) were calculated as the average level in the blanks plus three times the standard deviation of the blanks (Table 4.3). The LOD values ranged from 16.7 to 33.1 ng per sampler. LODs for cVMS on an ng per m^3 basis were calculated with the experimentally determined passive sampling rates and a sampling time of 10 days. LODs ranged from 7.2 to 16.8 ng per m^3.

Table 4.3. LOD values of passive sampler.

	D_4	**D_5**	**D_6**
LOD (ng per sampler)	19.8	33.1	16.7
LOD (ng m^{-3})	7.2	16.8	7.2

It was noted that the blank levels are relatively high and further improvements in the preparation methods of the passive samplers could potentially lower the blank levels further. For this method to be suitable for quantitative determination of cVMS in locations where concentrations are low, lowering blank values will be essential. For instance, pre-cleaning of the sorbents together with the bag after the heat-sealing step might be an important step to remove sources of cVMS contamination during the heat-sealing process. Over a period of 10 days, the passive uptake of cVMS appeared to remain linear however longer calibration studies would be necessary to establish the maximum linear phase for cVMS uptake by this passive sampling method.

4.11 Real indoor air sampling in homes

To validate the passive sampling method that has been developed, real indoor air sampling was carried out in homes of people in York. The aim of this work is to understand the ranges in the concentrations of cVMS detected in the indoor environment. Participants were provided with an information sheet and a consent form (see Appendix B) to be signed. The responses of participants were to remain confidential and anonymous.

Participants for the indoor air sampling were given a bottle containing a sampling bag filled with ENV+ sorbents (Figure 4-36). The sampling bags were removed from the vial and hung at home for 48 hours (2 days). After the sampling period, the sampling bags were put back into the vials and returned for analysis. Care was taken not to touch the sampling bags at any point.

Figure 4-36. Passive sampling bag in a sealed vial.

4.11.1 Calibration

Calibration standards were ran for D_3, D_4, D_5 and D_6 on the GC-TOFMS instrument. The R^2 values from the calibration curves for the compounds were acceptable at about 0.97 to 0.98 (Figure 4-37).

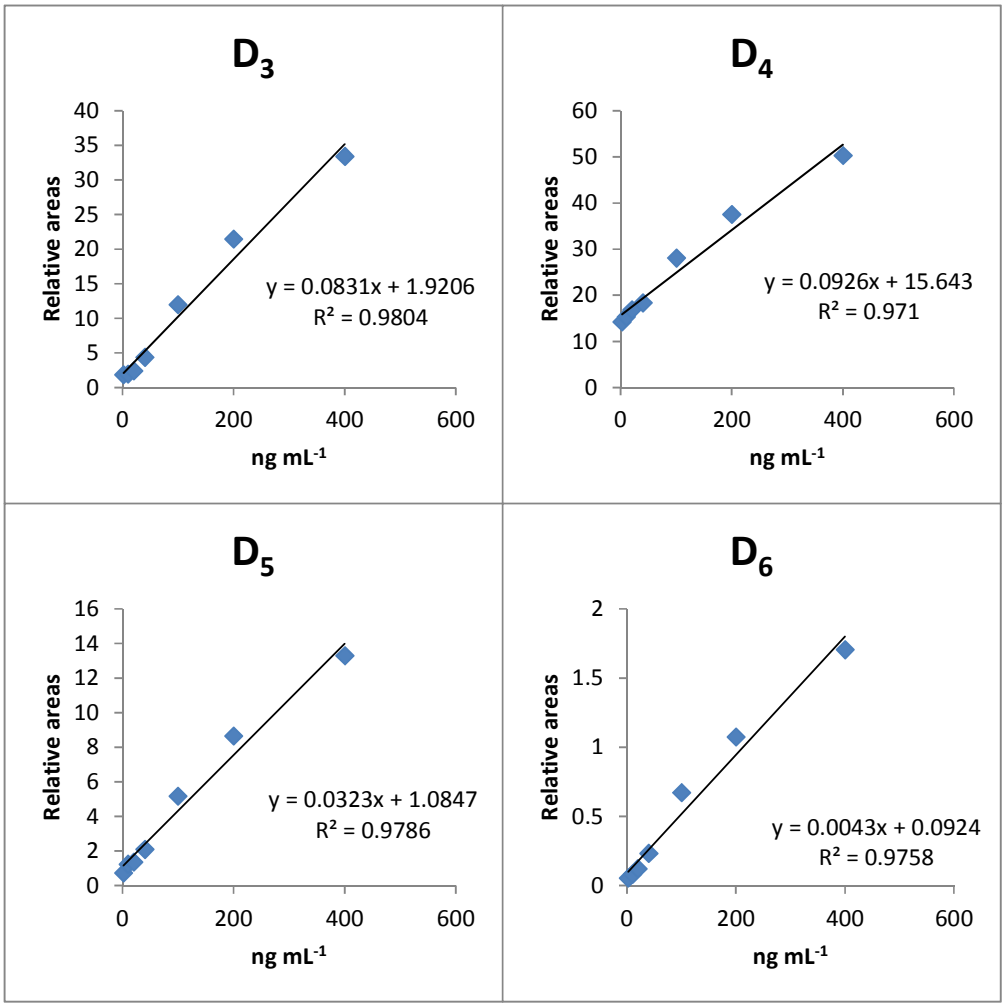


Figure 4-37. Calibration standards ran for D_3, D_4, D_5 and D_6.

4.11.2 Results from real indoor air analysis of cVMS

The sampling bags were analysed immediately upon return of the bags. As previously, the bags were extracted with 1 mL of DCM, with 30 µL of M4Q added to the vial before pipetting out to a GC vial for analysis by GC-TOFMS. In order to minimise contamination of the samples with cVMS, materials and

personal care products that contain cVMS were avoided during the sample preparation, handling, extraction, and analysis procedures.

Table 4.4 shows the results obtained for the analysis of cVMS in homes. All concentrations are corrected for blanks by subtracting the absolute amount of each individual cVMS from their amounts in the sample.

Concentrations of D_3, D_4, D_5 and D_6 were calculated based on their sampling rates of 0.26, 0.28, 0.20, 0.23 m^3 per sampler per day respectively (Figure 4-33).

Table 4.4. Concentrations of D_3, D_4, D_5 and D_6 in York homes.

Homes	Concentration (ng m^{-3})			
	D_3	D_4	D_5	D_6
01	97.1	232	5230	2280
02	N.D.	33.5	5270	3680
03	73.8	281	235	652
04	63.4	144	147	279
05	15.9	63.7	796	486
06	31.9	N.D.	5230	603
07	173	85.9	4900	N.D.
08	42.5	N.D.	5620	289
09	N.D.	N.D.	388	N.D.
10	N.D.	N.D.	109	N.D.
11	N.D.	48.2	6050	468
12	233	N.D.	150	N.D.
13	N.D.	N.D.	N.D.	N.D.
14	N.D.	N.D.	521	N.D.
15	99.3	168	2620	382
16	N.D.	N.D.	116	N.D.
17	19.1	N.D.	196	N.D.
18	16.0	265	3580	287
19	193	101	6030	2730

The limits of detection (LOD) were calculated as the average level in the blanks plus three times the standard deviation of the blanks. The LOD values ranged from 0.545 to 74.0 ng per sampler depending on the congener. LODs for cVMS on an ng per m^3 basis were calculated with the experimentally determined passive sampling rates and a sampling time of 2 days. LODs ranged from 1.38 to 159 ng per m^3 depending on the congener (Table 4.5). The previously established LOD values (Table 4.3) for D_4 and D_6 were lower by about 3 and 22 times respectively. Conversely for D_5, the previously established LOD value was about 12 times higher. The difference in the blank levels and hence the LOD values were likely due to the different instrumental systems, solvents, apparatus and set up used.

Table 4.5. LOD values for cVMS analysis.

	D_3	**D_4**	**D_5**	**D_6**
LOD (ng per sampler)	6.19	12.0	0.545	74.0
LOD (ng m^{-3})	11.9	21.8	1.38	159
1/2 LOD (ng m^{-3})*	5.96	10.9	0.691	79.4

Table 4.6. Mininum, maximum and average concentrations of cVMS in homes.

	Concentration (ng m^{-3})			
	D_3	D_4	D_5	D_6
Min	ND	ND	ND	ND
Max	233	274	6050	3680
Average*	57.7 ± 16	79.6 ± 21.2	2480 ± 579	664 ± 238

*in the calculation of averages, the N.D. are taken to be 1/2 the LOD. The N.D. values will lie somewhere in between the LOD value and 0, so 1/2 LOD value is taken to be the average value for N.D. situations.

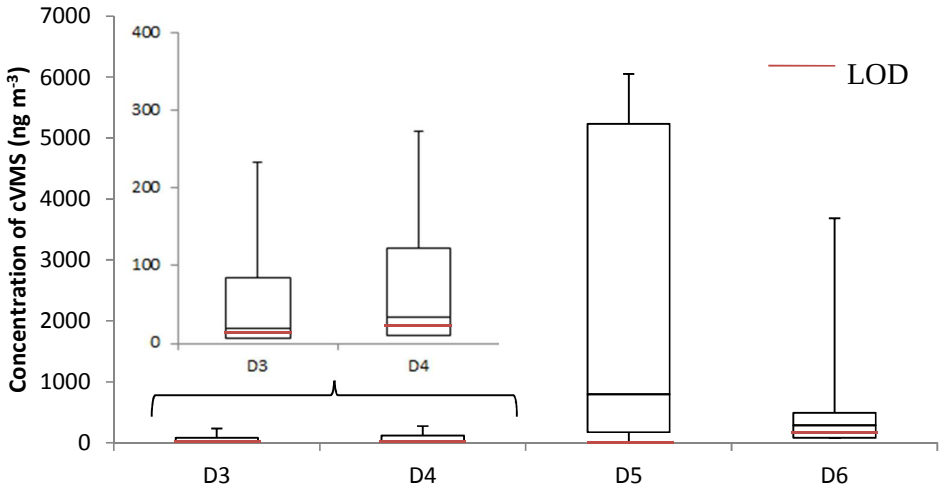


Figure 4-38. Box and whiskers diagram showing the median and interquartile range of the concentration of cVMS in samples of homes analysed.

The concentrations of individual cVMS ranged from below detection limits for all the compounds to as high as 6050 ng m^{-3} for D_5 (Table 4.6). In most of the homes, D_5 was the most abundant cVMS, followed by D_6. This was expected as D_5 and D_6 (with D_5 being the most) are widely used in consumer products [69, 71].

A direct analysis method of cVMS using atmospheric pressure chemical ionisation-tandem mass spectrometry (APCI-MS/MS) has been reported previously [172]. This method will not face the contamination problems associated with the use of GC, i.e. septum contamination and thermal or oxidative degradation of the polysiloxane-based stationary phases of the GC column. However, the LOD reported for this method of analysis is 6 µg m^{-3} and 4 µg m^{-3} for D_4 and D_5 respectively [172] which are values higher than the typical ambient air concentrations [74, 75, 162, 171]. The direct analysis method was used for the analysis of landfill biogas samples, with mean concentrations of D_4 and D_5 determined to be 257 – 7850 µg m^{-3} and 16.5 – 107 µg m^{-3} respectively.

Companioni-Damas et al. detected D_5 as the most abundant methyl siloxane in indoor air, with average concentrations ranging from 1700 – 293000 ng m^{-3} using Isolute ENV+ sorbent as the sorbent for active sampling, combined with concurrent solvent recondensation – large volume injection – gas chromatography – mass spectrometry (CSR-LVI-GC-MS) [76]. CSR-LVI technique was applied to increase the sensitivity of the method and avoid concentration procedures of the sample to minimise loss of smaller mass compounds via volatilisation. With this method of analysis, LOD values of as low as 0.08 – 0.15 ng m^{-3} were achieved for D_3 – D_6 [76].

There have been analyses of indoor concentrations of cVMS using active sampling methods. In a study conducted by Pieri et al. [164], it was found that the most abundant chemical in almost all the homes samples in Italy and UK was D_5; average D_5 concentrations were 38 – 170 µg m^{-3} in Italy, and 45 – 150 µg m^{-3} in UK. Their indoor air sampling employed is an active sampling method involving the use of sorbent tubes and air-pump to draw air through the sampling tubes. These concentrations were about 1 – 2 orders of magnitude higher than in this work. In another study conducted by Yucuis et al. [81], D_5 was also the dominant cVMS found in an indoor environment. Indoor air samples were collected in laboratories and offices at the University of Iowa, USA, with D_5 concentrations ranging from 0.97 – 56 µg m^{-3}. The sampling means employed was also an active sampling method, involving the use of a diaphragm pump to draw air through sorbent-contained cartridges. Tran et al. carried out the sampling of indoor air in various locations in New York, USA, using polyurethane foam (PUF) plugs packed in a glass tube and collection of indoor air samples were by a low-volume air sampler [173]. Similar to previous studies, D_5 was found to be the most abundant in the indoor air samples, with an average concentration of 263 ng m^{-3} in homes [173]. The ranges in the concentrations measured reflected the wide variations of D_5 concentrations in the indoor environment which could be affected by factors such

as occupancy, period of sampling, location of sampling, amount and types of consumer products used. In a study by Tang et al., it was stated that emissions of cVMS occurred as a "burst" source with the entrance of an occupant [83]. It was suggested that while the amount and types of products used by occupants affected the variability in the concentration of cVMS detected, enhanced emissions might be due to wearing of outer layers of clothing that were removed when indoors, resulting in the burst of emissions [83].

There have been passive sampling techniques applied for the analysis of cVMS in outdoor environments. Krogseth et al. reports the calibration and application of using a polystyrene-divinylbenzene copolymeric resin (XAD) as a sorbent for the passive sampling and analysis of cVMS [78]. The sampling rates reported were between 0.4 – 0.5 m^3 per day, which were about 2 times higher than the passive samplers developed here. Samplings were conducted outdoors in rural areas, urban region and at sewage treatment plants. The cVMS concentrations in rural areas were found to be below LOD for D_3, D_4, D_5 and D_6 (LOD values of 22.5, 10.7, 25.0 and 21.7 ng m^{-3} respectively); in urban sites, the average concentrations of D_4 and D_5 were about 41 ng m^{-3} and 122 ng m^{-3} respectively.

Another passive sampling method uses sorbent-impregnated polyurethane foam (SIP) disks. These SIP disks are PUF disks impregnated with XAD resin. In the studies involving the use of SIP disks, the sampling rates were reported to be 3.1 – 3.7 m^3 per day [174], 4.1 – 5.7 m^3 per day [79] and about 6.5 m^3 per day [77]. These sampling rates were more than 1 order of magnitude higher than that reported in this work. The samplings were conducted at a semiurban area [79], at wastewater treatment plants and landfills [174], and in urban, background and Arctic sites [77]. D_5 was found to be the most abundant cVMS with average concentrations of about 140 ng m^{-3} at the semiurban site, and 812 – 5380 ng m^{-3} at wastewater treatment plants. In the study by Genualdi et al., D_5 dominated the levels of cVMS in the

urban sites at concentrations ranging from 55 – 280 ng m^{-3}, whereas D_3 and D_4 dominated the background and Arctic sites with concentrations ranging from below detection limit to 44 ng m^{-3} [77].

Concentrations of cVMS outdoors are influenced by meteorological conditions such as wind speed and direction, ambient temperature. In the study by Lutz et al., it was found that while there was no significant relationship between concentrations and precipitation or relative humidity, wind direction and wind speed were significant factors affecting the concentrations measured in air; high concentrations were observed to be correlated to a wind from a certain direction, indicating a higher level a contamination in air from urban and industrial areas [79].

The concentrations of the indoor homes detected in this study were relatively higher than that of outdoors at semiurban and urban sites. This was in accordance to the expectation of higher indoor air concentrations of cVMS because of the prevalence of consumer products predominantly containing cVMS and their accumulation in indoor areas.

Table 4.7 shows the tabulated mean cVMS concentrations of the mentioned studies.

Table 4.7. List of cVMS concentrations at various locations with different sampling and analysis methods.

	Mean concentrations (ng m^{-3})					
Location	D_3	D_4	D_5	D_6	Method	Reference
Landfill	-	257000 – 7850000	16500 – 107000	-	Direct APCI-MS/MS	172
Urban outdoor	2.2 – 5.0	73 – 76	375 – 439	45 – 60	Active sampling with ENV+ SPE cartridges; CSR-LVI-GC-MS	76
Indoor (offices and homes)	48 – 170	226 – 3050	1700 – 293000	156 – 84600	Active sampling with ENV+ SPE cartridges; CSR-LVI-GC-MS	76
Indoor (homes, Italy)	3500 – 69000	8000 – 42000	38000 – 170000	1000 – 45000	Active sampling with sorbent tubes; TD-GC-MS	164
Indoor (homes, UK)	1200 – 160000	1900 – 68000	45000 – 150000	5400 – 26000	Active sampling with sorbent tubes; TD-GC-MS	164
Indoor (offices and laboratories)	-	23 – 500	970 – 56000	nd – 2800	Active sampling with ENV+ SPE cartridges; GC-MS	81
Indoor (homes)	21.6	50.9	263	50.9	Active sampling with PUF plugs packed in glass tubes; GC-MS	173

Urban outdoor	nd (below LOD)	41 ± 12	122 ± 39	nd (below LOD)	Passive sampling with XAD in mesh cylinders; GC-MS	78
Wastewater treatment plants	2.19 – 268	241 – 2060	812 – 5380	32 – 253	Passive sampling with SIP (XAD-PUF) disks; GC-MS	174
Semiurban outdoors	1.4 ± 0.7	21 ± 8.3	140 ± 24	11 ± 3.3	Passive sampling with SIP (XAD-PUF) disks; GC-MS	79
Urban outdoors	0.65 – 30	5.4 – 50	55 – 280	4.0 – 53	Passive sampling with SIP (XAD-PUF) disks; GC-MS	77
Background outdoors and artic	nd – 117	nd – 45	nd – 96	nd – 12	Passive sampling with SIP (XAD-PUF) disks; GC-MS	77
This study	57.7 ± 16	79.6 ± 21.2	2480 ± 579	664 ± 238	Passive sampling bags containing ENV+ sorbents	-

4.12 Conclusion

The development of this simple passive sampling method for the analysis of indoor cVMS allows for the simple, low cost and non-intrusive collection of a large number of samples from indoor environments such as homes or offices. The method achieved acceptable degrees of reproducibility and sensitivity and offers a route to the quantification of cVMS in the built environment as well as a means to assess a variety of possible emissions and impacts for such compounds.

Further work could be done with these passive samplers. Correlation studies could be conducted. For instance, the relationships between occupancy and concentration of cVMS observed, or the amount of time spent at home and the concentration of cVMS observed could be studied. In addition, source attribution studies could also be carried out. Details, such as the types of personal care products and consumer products used and their frequency of usage during sampling, have to be collected for source attribution studies. Samplers could also be placed in different locations in the homes i.e. bathrooms, kitchen, women's bedroom, men's bedroom, to see if there are any interesting observations of cVMS concentrations that may be room / activity dependent.

Chapter 5

Development of a portable sensor device: Heating and detection

5.1 Introduction

This chapter describes the work that has been carried out with regards to the development of a gas chromatography lab-on-a-chip (GC-LOC) sensor.

The current laboratory set-up for the detection and analysis of VOCs includes a thermal desorption unit, followed by the commonly used GC and detection method, such as the flame ionisation detector (FID) or mass spectrometer (MS). These laboratory instruments are standard measurement techniques that have proved to be efficient, straightforward and accurate for the analysis of VOCs. However, the size, mass and power requirements of these laboratory instruments render them unsuitable for use out of the laboratory. Hence, there is a need for the development of a portable device that provides reliable information for the field measurements of a range of different VOCs.

The development of the portable in this work is essentially made up of a few components: i) a thermal desorption method for the pre-concentration of analytes, ii) a column for the separation of different compounds in a mixture, iii) a temperature control (heating and cooling) means for the effective separation of compounds in the column, and finally iv) a detector. Figure 5-1 shows a schematic outline of the proposed work for the sensor development. This chapter will describe in more detail on the temperature control method and the detector used in the development of a portable sensor.

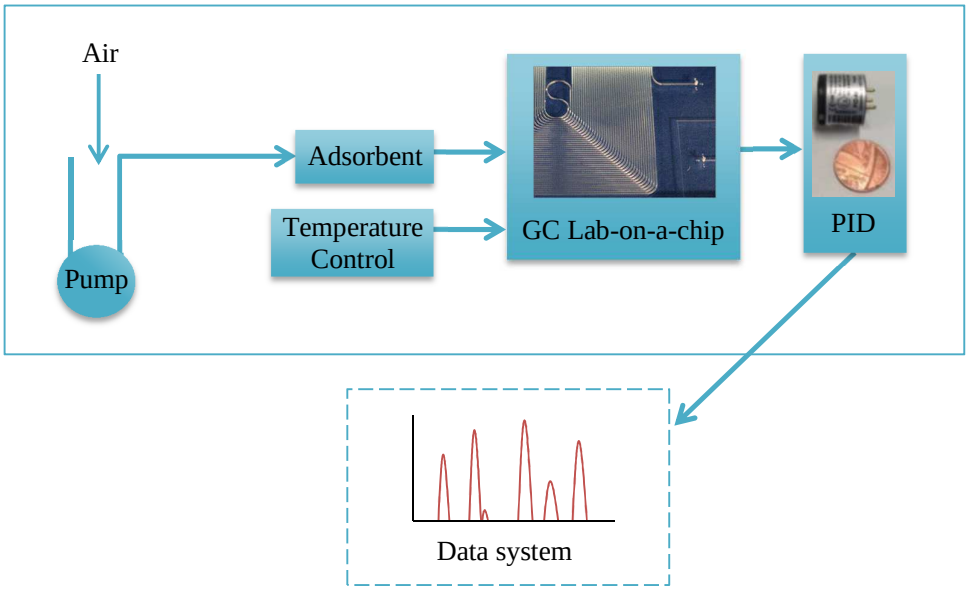


Figure 5-1. Schematic diagram for sensor development.

5.2 Heating and cooling of the GC column

One important factor for an effective GC separation is the uniform heating of the GC column and the ability to increase this temperature linearly to elute higher boiling compounds sequentially. The heating of GC columns by conventional means is primarily based on the turbulent fan oven, which is an excellent means to achieve even heating of the column. However the size of such ovens renders this a difficult technique to use in remote locations for field analysis in environmental research. In addition, the power consumption is high and of the order of 1.5 kW for a typical 10 ^{o}C min^{-1} heating rate.

The fabrication of a GC-LOC is likely to be of a flat and planar structure, allowing a structural geometry that is much easier to heat using planar devices, such as a Peltier device (Figure 5-2) which could be placed on the surface of the fabricated chip. The Peltier device is small, light and inexpensive, and hence is a

practical means as a temperature control method for the development of a portable sensor. One with the dimensions of 40 x 40 x 3.45 mm (length x width x thickness) was purchased for our purpose.

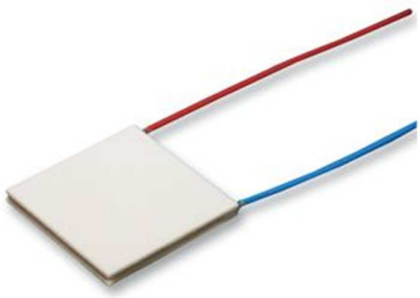


Figure 5-2. Peltier device.

When a voltage is applied and current flows through the junctions of the Peltier device, one side of the Peltier device loses heat while the other side absorbs heat. When the polarity of the voltage is switched, the heating and cooling effect of the Peltier device is switched to the other side as well. The heat generated has to be removed with a heatsink and a fan. Figure 5-3 shows an example of how the Peltier device can be placed together with a heatsink and a fan. The operating temperature of this Peltier device can go as low as -40 °C. Hence, an advantage of using the Peltier device is that it allows the starting temperature to be below room temperature, allowing the improved separation of volatile VOCs without the need for cryogenic cooling as used in standard GC ovens. To mimic the temperature control in existing GC ovens, it is essential that the temperature gradients and set points of the Peltier device can be manipulated to allow manual control of the device.

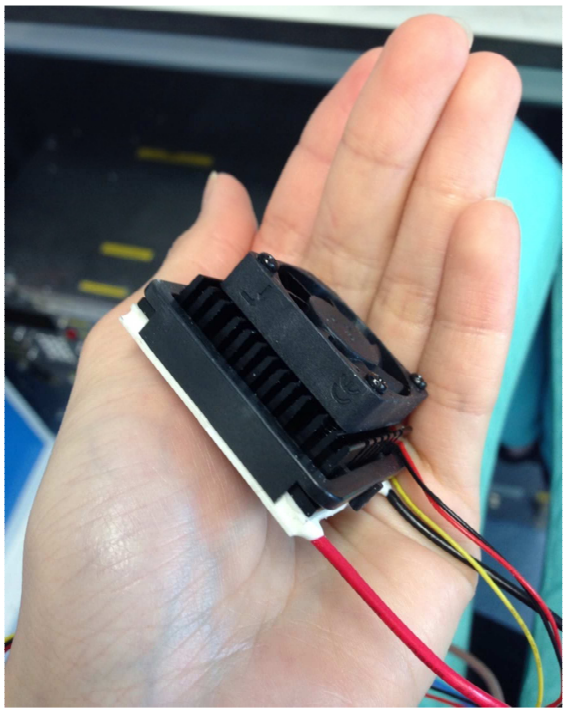


Figure 5-3. A Peltier device with a heatsink and a fan.

5.2.1 Temperature control of the Peltier device

A program is designed using LABVIEW to control the temperature, i.e. the set points and gradients, of a Peltier device. A block diagram containing the code for this temperature control can be found in Appendix C. It was estimated that a functional working range of temperature should be from 10 °C to 100 °C, which broadly mimics in terms of peak capacities a standard separation of VOCs performed over 40 °C to 150 °C. The Peltier device is used as both a heater and a cooler, with a switch over between cooling and heating achieved via a polarity reversal in the d.c. supply. The control software essentially mimics a standard GC bringing the temperature of the device to an initial value (10 °C), holding it there, and then ramping the temperature at a given rate (10 °C min^{-1}) until the final temperature is reached (100 °C) before cooling back down to 30 °C. This is

achieved through Proportional Integral Derivative control. Figure 5-4 shows the result of the one temperature cycle test. The program produces a desired set point temperature profile (blue graph) and adjusts the power supplied to the Peltier device to bring the temperature of the device (red graph) to this value. The Peltier device is fitted with a heat sink and fan as it requires cooling.

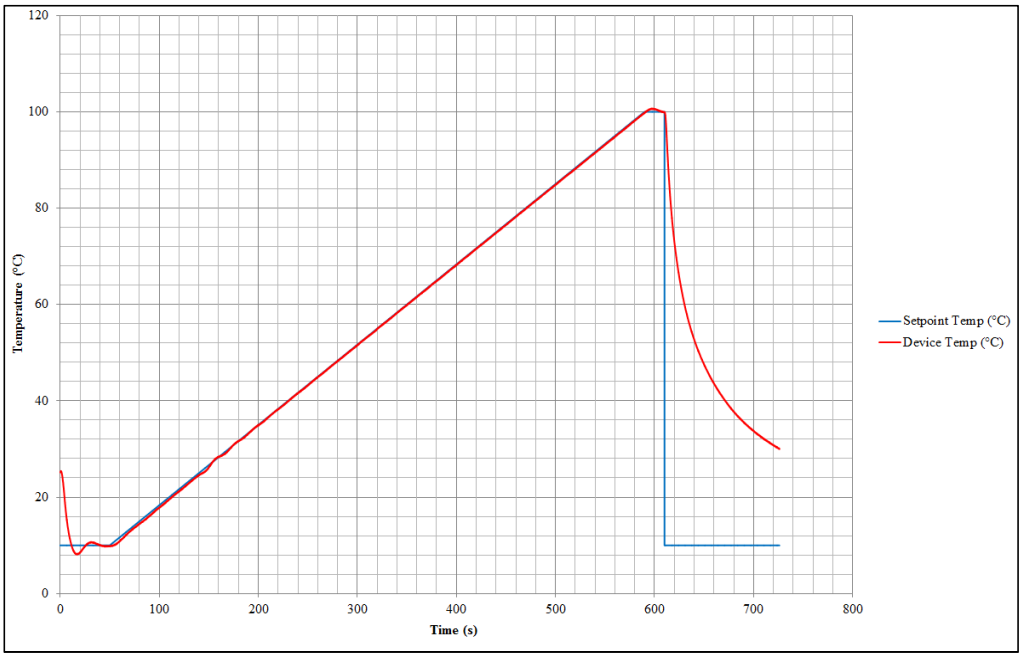


Figure 5-4. One temperature cycle of the Peltier device.

To test the performance of the Peltier device for continuous sequential runs, five such temperature cycles were set to run and the resulting temperature profiles are shown in Figure 5-5. It was noted that the set point and device temperatures were almost identical for the majority of each ramp and that there was no thermal wind-up in the system – that is the starting 10 °C could be achieved reproducibly each time.

Features of note are the slight overshoot at the initial and final temperatures, and the slight wobble through room temperature region as the voltage polarities are reversed. These can be optimised for a set of conditions, however in significantly different ambient conditions the Proportional Integral Derivative gains may need to be re-tuned if these differences to the set point become too large. As it is, the discrepancies are never more than about 1 °C (except the initial overshoot, which is often around 2 °C).

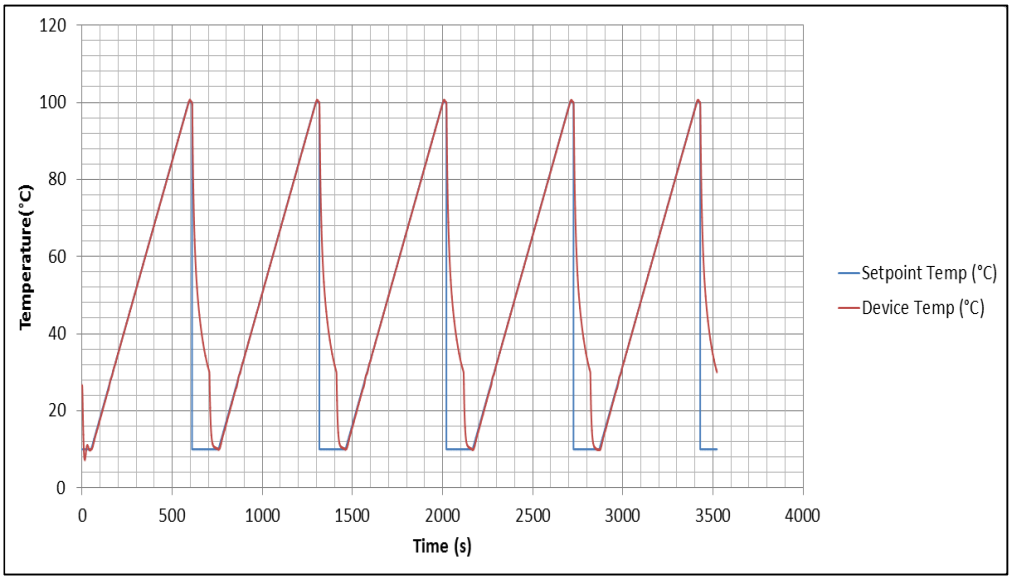


Figure 5-5. Five cycles of the Peltier device used for GC chip temperature control.

The total power used in this set up is about 40W, which relates to about 24 kJ per cycle of 10 minutes. This is a considerably lower power consumption compared to a laboratory gas chromatography oven which uses on average 1 kW over 30 minutes – that is, 1.8 MJ per cycle.

The set-up for the Peltier device together with the fans and heat sink are tentatively housed in a plastic container made in-house as shown in Figure 5-6.

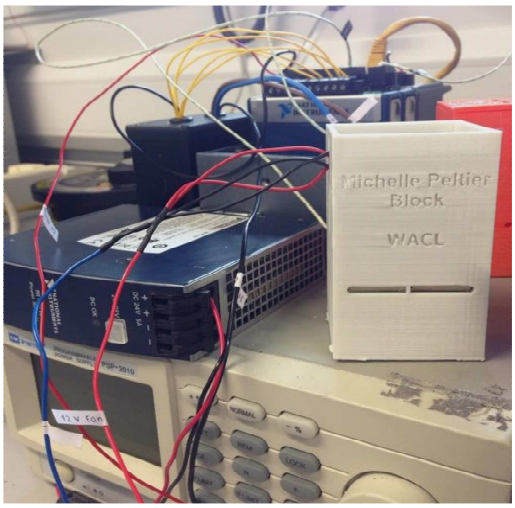


Figure 5-6. White container housing Peltier device and components

5.2.2 Summary of using Peltier device as a temperature control

The use of a Peltier device to control the temperature of a miniaturised GC column removes the dependence on the bulky and power hungry GC oven. We achieve precise control of the temperature set points and gradients of a Peltier based system through Proportional Integral Derivative control. A Peltier device with switchable polarities allows the initial temperature of the column to be as low as 10 °C, offering substantial advantages of the analysis of VOCs without the need for cryogenic cooling in standard GC ovens.

5.3 Separation performance of a laboratory GC-PID

A key barrier to portable GC systems has been a lack of a suitable detector for the field. The most simple lab detector is FID, but that is orientation specific and requires a hydrogen supply. Here we have focussed attention on a low-cost (~200 USD), commercially available photoionisation detector (PID) (PID-AH, Alphasense) as the detection method for VOCs measurement following GC. A picture of the PID is shown in Figure 5-7. The PID used here is designed

primarily for a solvent alarm, not a GC detector, so we have undertaken experiments to understand its capabilities if modified for this purpose. The ultraviolet (UV) lamp of the PID provided 10.6 eV for compound ionisation and the device was used as supplied, with the exception of the deliberate removal of a filter inlet placed over the detection grids.

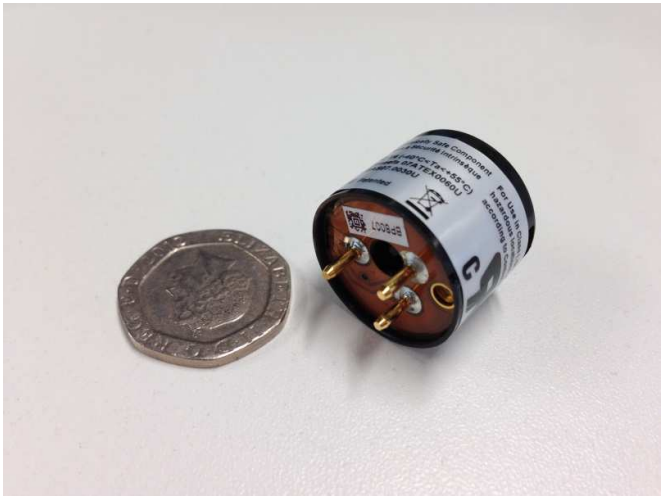


Figure 5-7. PID-AH purchased from Alphasense, placed next to a 20 pence for size comparison.

The UV lamp in the PID emits high energy protons onto a sample of ambient air drawn into the sensor chamber as shown in Figure 5-8 [175]. VOC compounds will be ionised into free electrons and positively charged ions if the photon energy from the UV light is greater than their ionisation potential. This produces an electric current which is a function of the concentration of ionised VOCs; the greater the concentration of VOCs in the air sample, the greater the current that will be generated and detected by the PID.

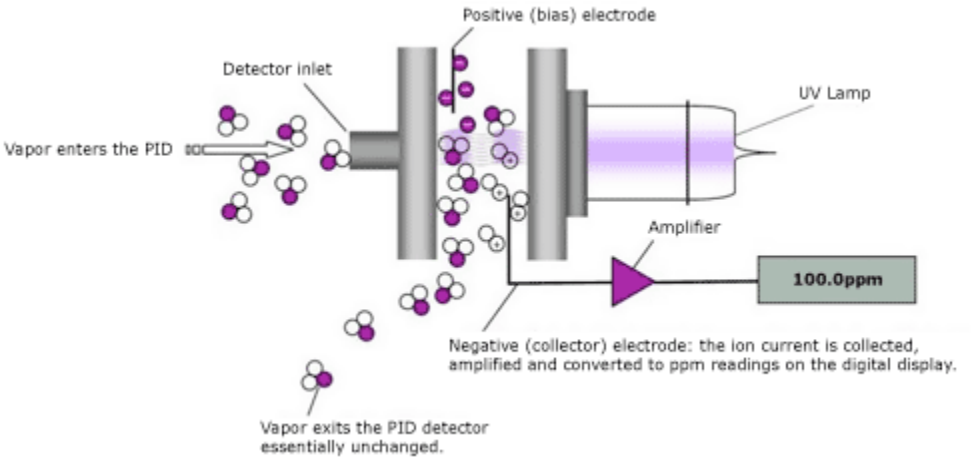


Figure 5-8. PID diagram.

High purity helium (BIP Air Products, Keumiee, Belgium) was used as the carrier gas for GC. Separation was performed on a BPX5 column (50 m x 0.32 mm x 1.0 µm, length x internal diameter x film thickness) with two split outlets, one going to a time-of-flight/mass spectrometer (TOF/MS) and the other going directly into the PID. This allowed for the comparison of the detector results of the PID with the TOF/MS. The oven was programmed to run at 40 °C for 3 minutes, then ramp at 15 °C min^{-1} to 125 °C, then at 20 °C min^{-1} to 250 °C and held for 5 minutes. Figure 5-9 shows how a capillary column is connected to the PID, and Figure 5-10 shows the actual and schematic set-up of the PID to the GC.

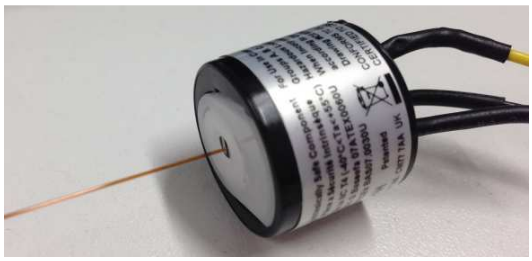


Figure 5-9. Capillary column connected to a PID.

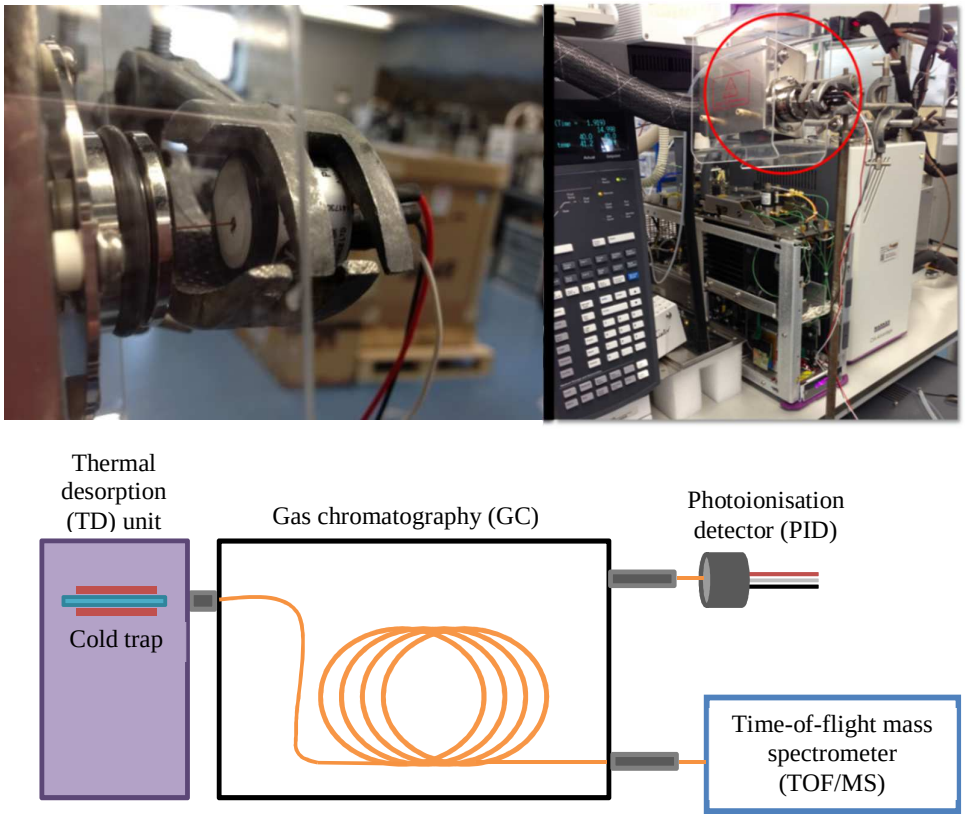


Figure 5-10. GC-PID set-up.

A standard mixture including 4 nmol/mol (molar ppb) of benzene, 2,2,4-trimethylpentane, heptane, toluene, octane, ethylbenzene, m-xylene, p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene was introduced into a thermal desorption unit (Markes Unity Series 2 Thermal Desorption Unit) prior to separation on the GC column. 1000 mL of gas was sampled at 100 mL min^{-1}. The trap was purged for 1 minute at 100 mL min^{-1} and heated from -30 °C to 300 °C at the maximum heating rate of the system and held for 3 minutes.

5.3.1 Data capture with 12-bit ADC LabJack

A commercially available hardware (LabJack U3-HV) was used as the analogue-to-digital converter (ADC). This ADC has a resolution of 12 bit. The results for detection with TOF/MS and PID are shown in Figure 5-11 and Figure 5-12 respectively. The results obtained with the PID shows good separation between the components with symmetrical peak shape comparable to that obtained with TOF/MS. The high PID response of the compounds gave a good signal to noise ratio. This PID chromatogram was generated with approximately 6.5 – 10 ng of each compound. Peak skew is less than 1.8 for all peaks (with half of them less than 1.2) which we considered acceptable. The chromatogram indicates around 67000 theoretical plates as measured for toluene. It is worth noting that this PID result was achieved without any direct heating of the PID itself.

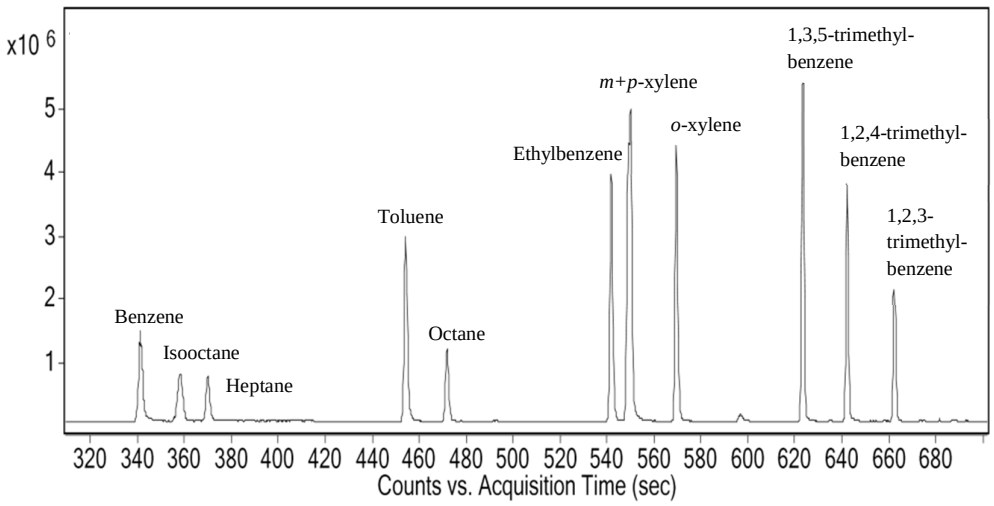


Figure 5-11. Separation of the 4 ppb standard gas mixture and detection by TOF/MS.

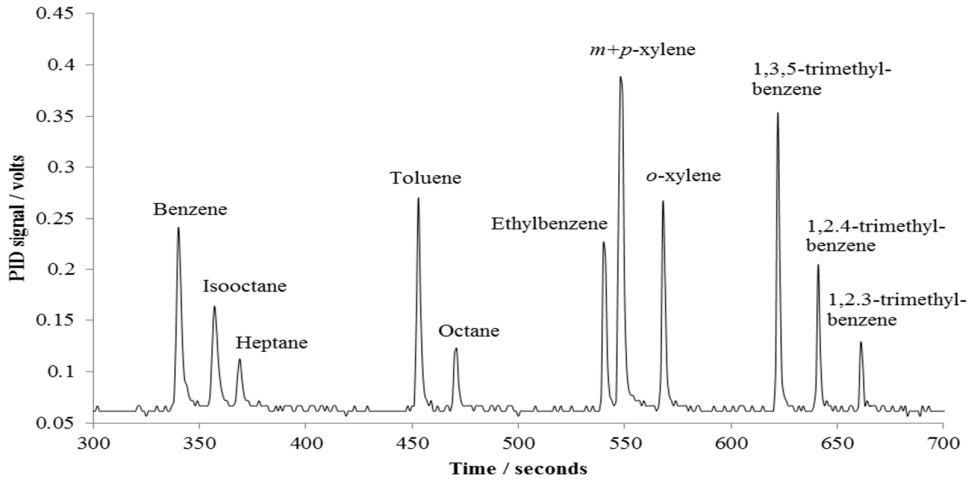


Figure 5-12. Separation of the 4 ppb standard gas mixture and detection by PID.

A second gas mixture containing approximately 26 ppb of isoprene and 77 ppb toluene was introduced separately. Parameters of the set up were identical to those used previously, but in this case only 100 mL of gas was sampled at 100 mL min^{-1}.

The results for detection with TOF/MS and PID are shown in Figure 5-13 and Figure 5-14 respectively. The results obtained with the PID shows symmetrical peak shape comparable to that obtained with TOF/MS. The high relative PID response of the compounds resulted in a good signal to noise at the ppb level. The PID chromatogram was generated with approximately 3.69 ng of isoprene and 14.78 ng of toluene at detector. Peak skew is around 1.0 for both compounds, with 68000 theoretical plates as measured for toluene.

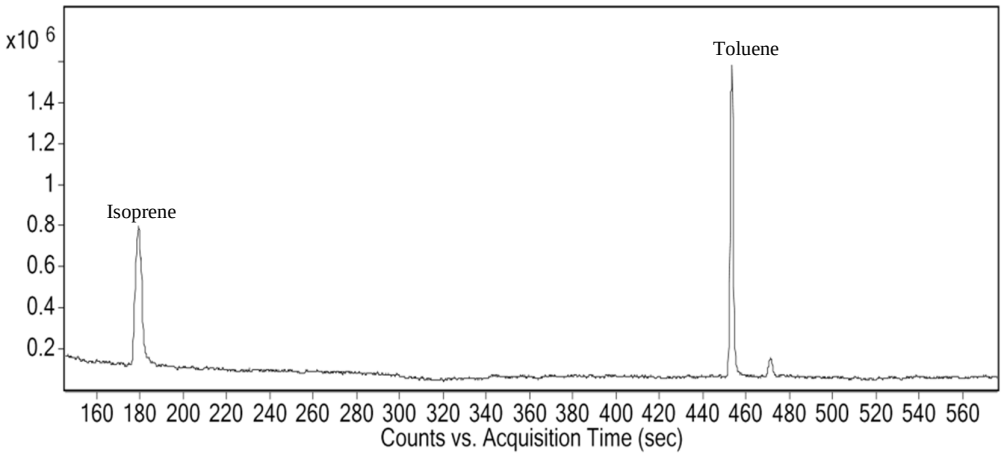


Figure 5-13. Separation of the isoprene and toluene gas mixture and detection by TOF/MS.

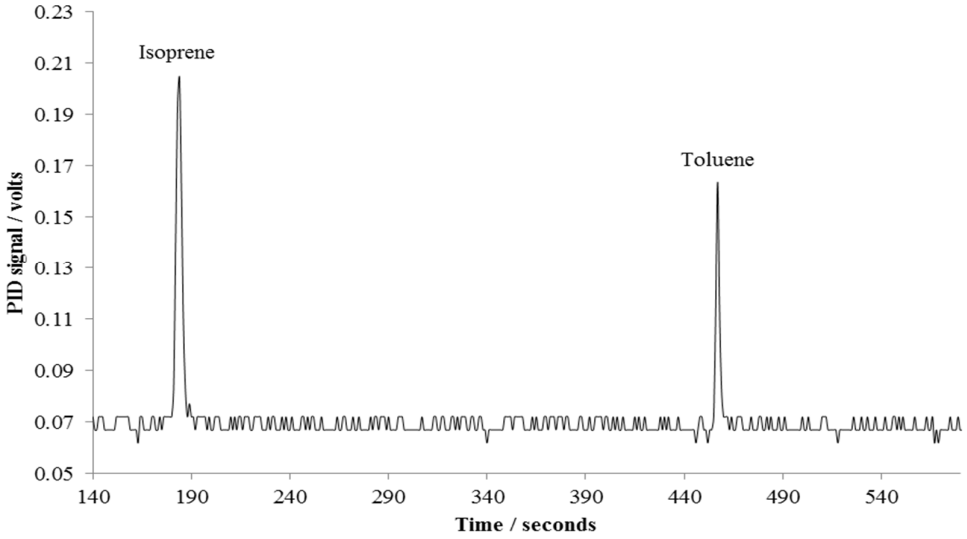


Figure 5-14. Separation of the isoprene and toluene gas mixture and detection by PID.

From the data obtained using the PID, digital noise could be observed at the baseline of the chromatograms (see Figure 5-14). The current analogue-to-digital converter (A/D) has a resolution of 12 bit. To improve the resolution of the data capture, future systems will use an A/D with a higher resolution of 18 bit.

5.3.2 Data capture with 18-bit ADC LabJack

Using a higher resolution data capture hardware, the digital noise observed previously at the baseline of the PID chromatograms had been eliminated. 1000 ml of the 4 nmol/mol standard gas mixture was sampled at the same conditions as described previously. The results for detection with TOF/MS and PID are shown in Figure 5-15 and Figure 5-16 respectively.

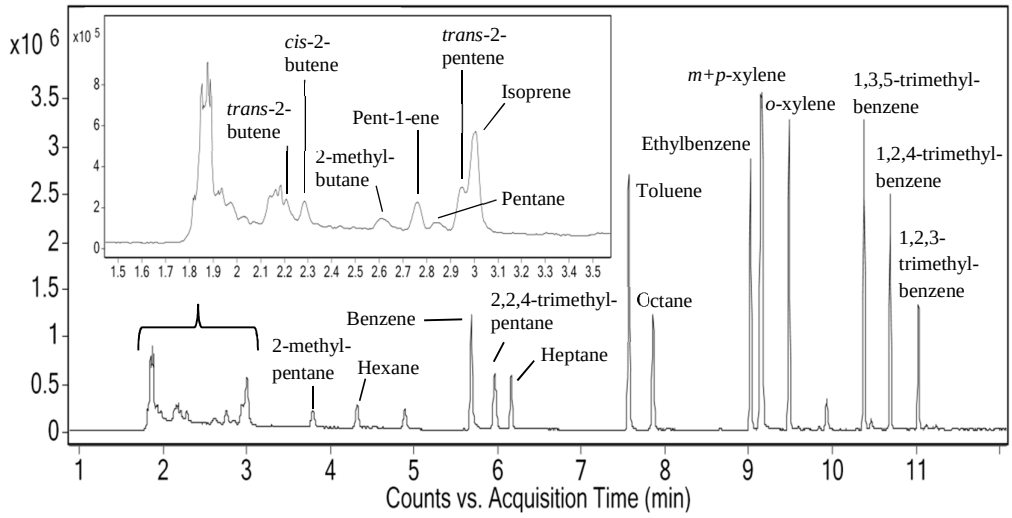


Figure 5-15. Separation of the 4 ppb standard gas mixture and detection by TOF/MS.

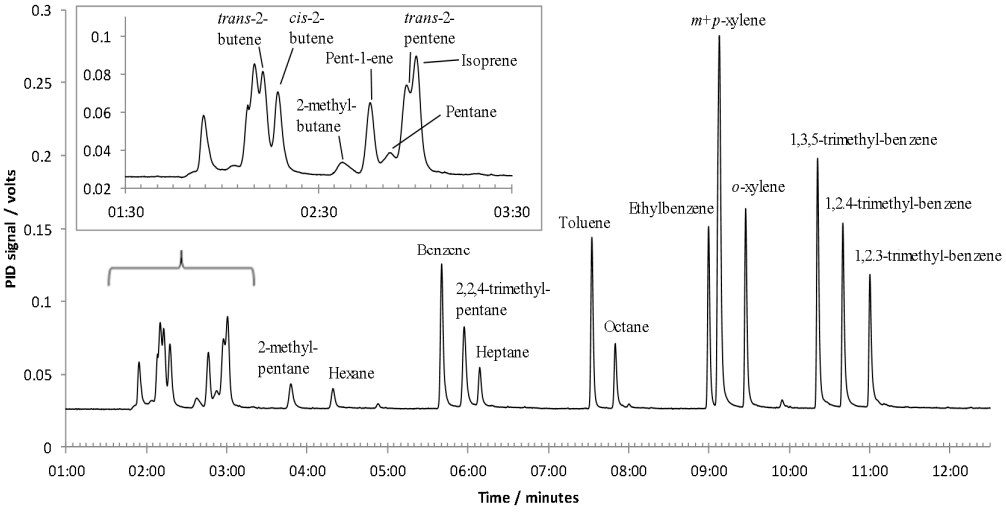


Figure 5-16. Separation of the 4 ppb standard gas mixture and detection by PID with 18-bit ADC.

Compounds with retention times before that of benzene are allocated to their respective peaks based on information obtained from their mass spectra and their boiling points. It was observed from the enlarged chromatograms of the early eluting peaks that the resolution of the peaks from the PID were comparable to, if not better than, that of the TOF/MS. This is because the MS may not be as proficient in detection of compounds with smaller masses; the smaller compounds are fragmented to even smaller masses which "disappear" into the background of the chromatograms.

With the elimination of the digital noise at the baseline of the PID chromatograms, the limit of detection (LOD) of the PID detection method could then be evaluated. 200 mL of the 4 nmol mol^{-1} standard gas mixture was sampled at the same conditions as described previously. The result for detection with PID is shown in Figure 5-17.

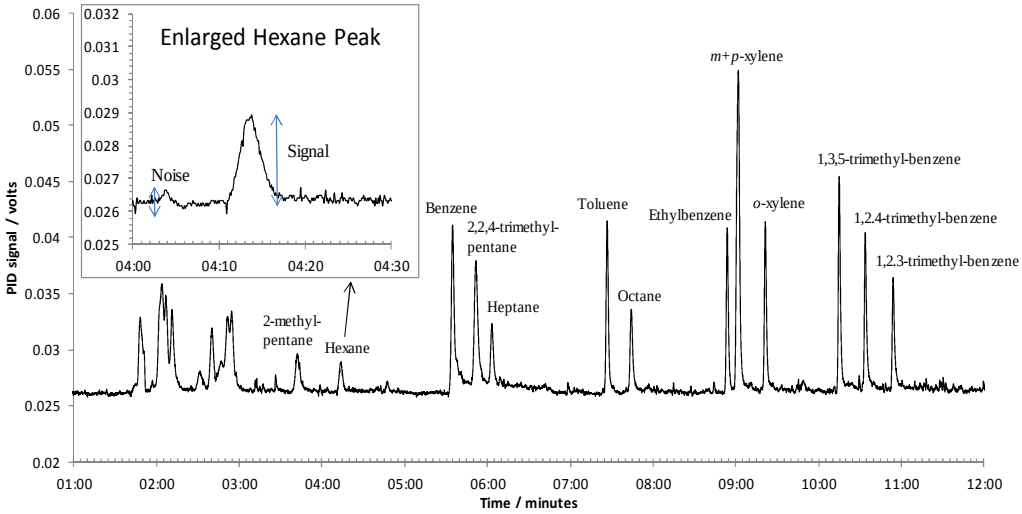


Figure 5-17. Separation of the 4 ppb standard gas mixture and detection by PID.

The signal to noise ratio for hexane in the sampling of 200 mL of the 4 nmol mol^{-1} standard mixture is about 3:1. Hence the LOD of hexane for this described method of detection is about 1.4 ng. The LOD for the other compounds were calculated based on extrapolation from the LOD of hexane and the values are tabulated as shown in Table 5.1.

Table 5.1. LOD of compounds with PID as detection method.

Compounds	LOD (ng)	LOD (ng s^{-1})	LOD (ppb)
2-methylpentane	1.2	0.24	0.34
Hexane	1.4	0.24	0.40
Benzene	0.29	0.19	0.088
2,2,4-trimethylpentane	0.55	0.24	0.12
Heptane	0.97	0.33	0.23
Toluene	0.32	0.38	0.085
Octane	0.87	0.38	0.18
Ethylbenzene	0.40	0.35	0.090
m+*p*-xylene	0.41	0.51	0.046
o-xylene	0.38	0.35	0.086
1,3,5-trimethylbenzene	0.34	0.33	0.069
1,2,4-trimethylbenzene	0.47	0.33	0.094
1,2,3-trimethylbenzene	0.67	0.33	0.13

Table 5.1 also includes the LOD (ng s^{-1}) based on a sampling amount of 200 ml. In this calculation, the absolute amounts (ng) of the compounds sampled were divided by their peak widths (seconds). The LOD in concentration (ppb) of the listed compounds were also calculated assuming a sampling of 1 litre of air for analysis.

5.3.3 Summary of using PID as the detector method

PID was chosen as the detector in this work as it offers substantial potential for the development of a field portable air quality sensor. When paired with a commercial GC system, the peaks produced by the PID were comparable to those produced by the TOF/MS, with acceptable peak skews and theoretical plates of >65000 for toluene. Peak tailing was observed to be minimal. These experiments highlighted the need for relatively high resolution data capture in order to fully exploit the inherent sensitivity of the PID. With the 18-bit data capture hardware, the digital noise observed previously at the baseline of the PID chromatograms had been eliminated. The LOD for the PID detection method was evaluated to be about 0.3 – 1.4 ng for the various compounds present in the standard mixture.

Chapter 6

Development of a portable sensor device: Columns and separations

6.1 Preliminary LOC design

The simple design for a GC – LOC column arrangement is as shown in Figure 6-1. The device is etched in a planar form which facilitates heating of the GC-LOC with a Peltier thermoelectric device [111], rather than the much higher power of a standard turbulent fan oven. A secondary advantage of a Peltier controlled device is an ability to operate below ambient temperatures, something not achievable in a fan oven without cryogenic cooling. The chip design is formatted to the same shape as existing Peltier devices commonly available at low cost. The design here uses two wafers, with etched channels on one side, bonded together to form a single chip. A number of different materials can be potentially used including glass, acrylic and PDMS. Prototyping using PDMS provides a quick and cost-efficient way of testing the feasibility of the GC-LOC design and is the initial route taken. It is proposed that the 45 x 45 mm chip will have an etch depth of a 150 µm semi-circle on one side; etches will be spaced 100 µm apart and the capillary will have a total length of about 4 – 6 m.

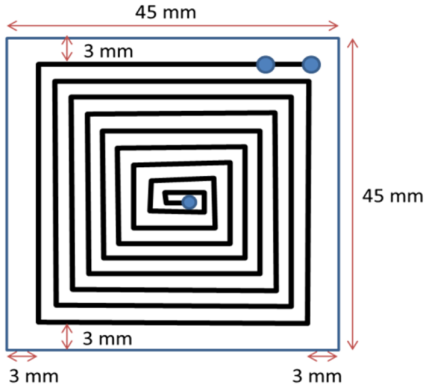


Figure 6-1. Preliminary design of GC – LOC on square-shaped chip.

6.1.1 First set of PDMS LOC

Some etched columns on PDMS (Scientific Device, USA) were made by soft lithography fabrication and bonded to a piece of glass. The characterisation of the GC-LOC has been carried out; National Physical Laboratory (NPL) looked at the chip under a microscope (x5 and x20 magnification). These LOCs have column widths of about 20 µm. There were some minor fabrication defects that were small and sporadic visible at x20 magnification (see Figure 6-4). The capillary length was estimated to be about 6.1 m.

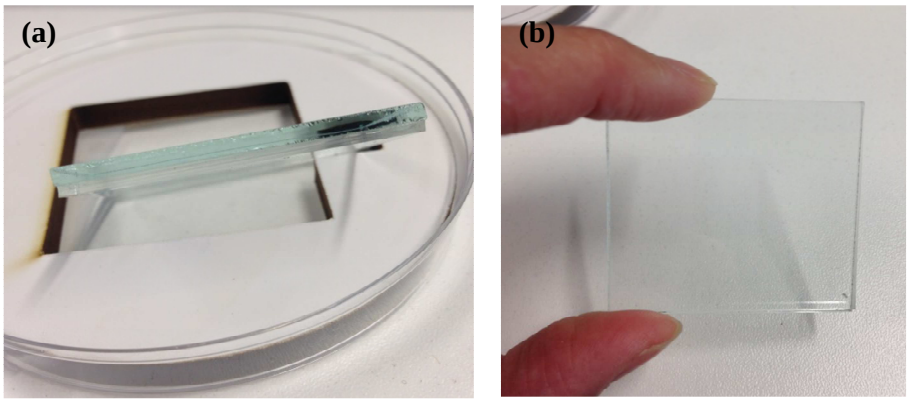


Figure 6-2. (a) Side view of PDMS chip. (b) Top view of PDMS chip.

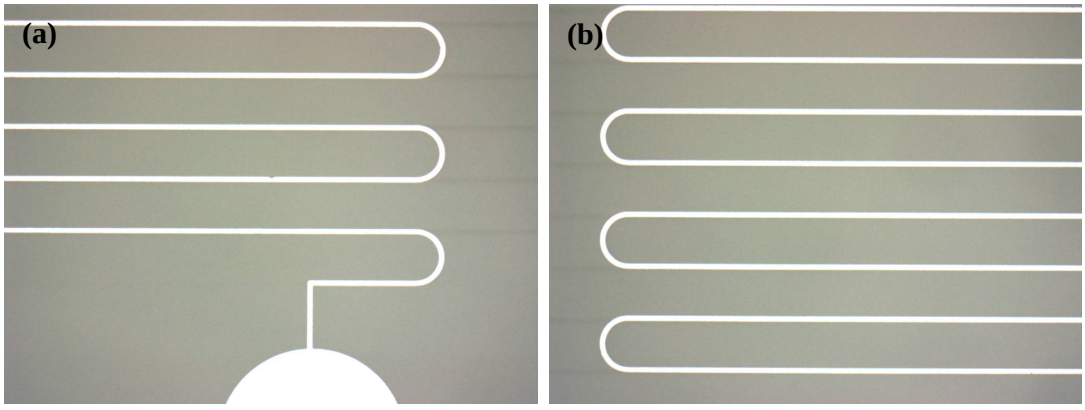


Figure 6-3. 5x magnification of PDMS chip.

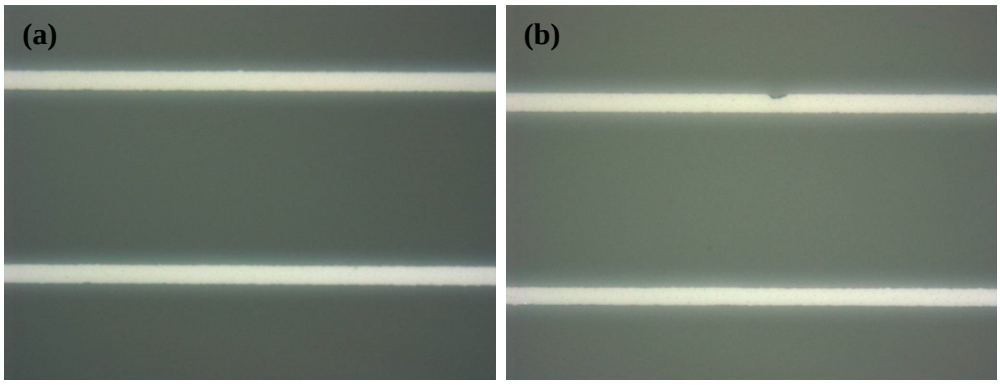


Figure 6-4. (a) 20x magnification showing good consistency in the channels. (b) 20x magnification showing minor fabrication defects.

It was necessary to first test if the PDMS was gas tight. For that to take place, a metal needle had to be fixed to the PDMS inlet to allow the introduction of gas into the columns. With PDMS as the attachment material, it was difficult to affix a connection needle; thermal bonding and epoxy did not work. It was hypothesized that the PDMS surface had to be activated before anything can bond with it. For the local activation of PDMS, oxygen plasma treatment or a localised oxidation method would be required. In an attempt to locally oxidised the point of contact with the connection needle, solution oxidation with H_2O, H_2O_2 and HCl in 5:1:1 proportion [176] was carried out. However, this method was not successful for bonding. It was decided that the next batch of PDMS chips be manufactured with needles already affixed at the inlet and outlet to eliminate the need to carry out post-activation of the PDMS after the manufacture.

A second set of etched PDMS chips were made. These LOCs have column widths of about 200 µm, and came with metal needles fixed to the inlet and outlet of the column channels.

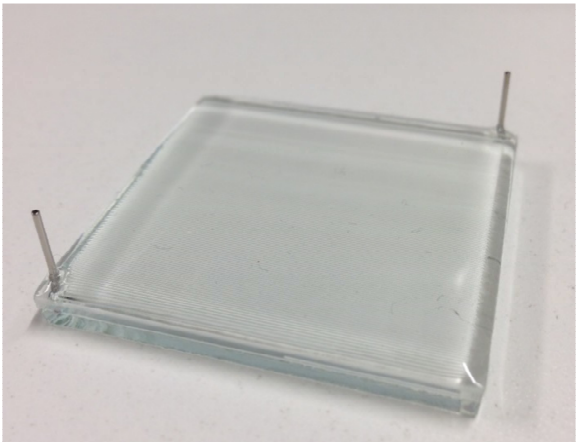


Figure 6-5. PDMS chip with needles fixed to the inlet and outlet of channels.

The needles attached to the PDMS chip were too short to allow any interconnections using column connectors or tube fittings. It was proposed that an extension of the needles was required to allow for fittings to be attached to the inlet. Due to the fragile nature of the attachment of the needle to the PDMS, it was decided that a more flexible PEEK tubing be attached to the needle to extend the working length of the inlet.

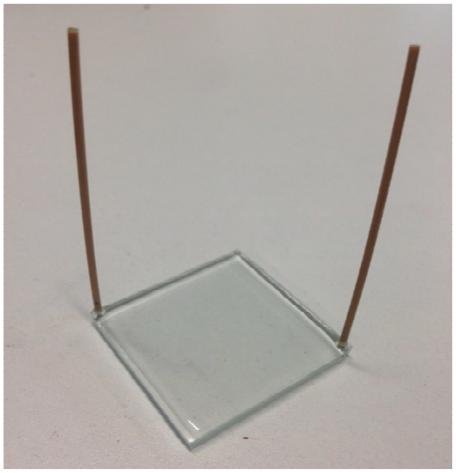


Figure 6-6. PDMS chip with PEEK tubing extensions at the inlet and outlet.

A leak test was carried out by introducing helium to the PDMS chip via a Swagelok connection at the PEEK tubing. However, due to the fragility of the needle attachment to the PDMS layer, the needle was easily displaced from the PDMS. Leakage of helium gas was also detected at the interface between the PDMS and the glass layer, and especially at the weak points where the needle inlet and outlet were placed.

6.2 Copper enclosure to contain GC column

A copper enclosure was made by the mechanical laboratory in the Chemistry department as an alternative to the PDMS GC LOC. The material of the enclosure was chosen to be copper as it has very good thermal conductivity, thus allowing efficient heat transfer between the enclosure and the Peltier device. A DB-5 column (6 m x 0.18 mm x 0.18 µm, length x internal diameter x film thickness) was wound and fitted into the enclosure, which was then placed in contact with the Peltier device.

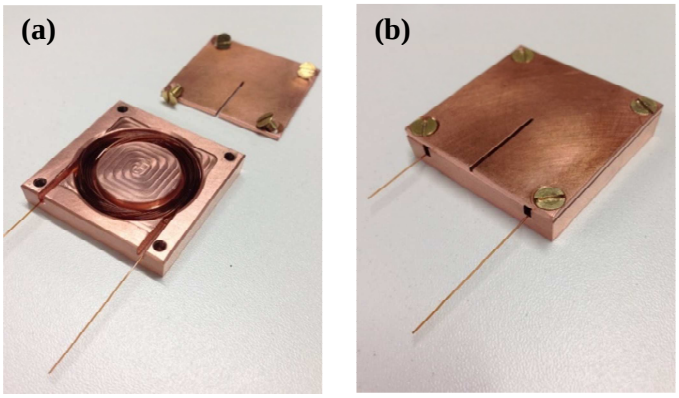


Figure 6-7. (a) Copper enclosure with column. (b) Copper enclosure, containing column, covered with lid.

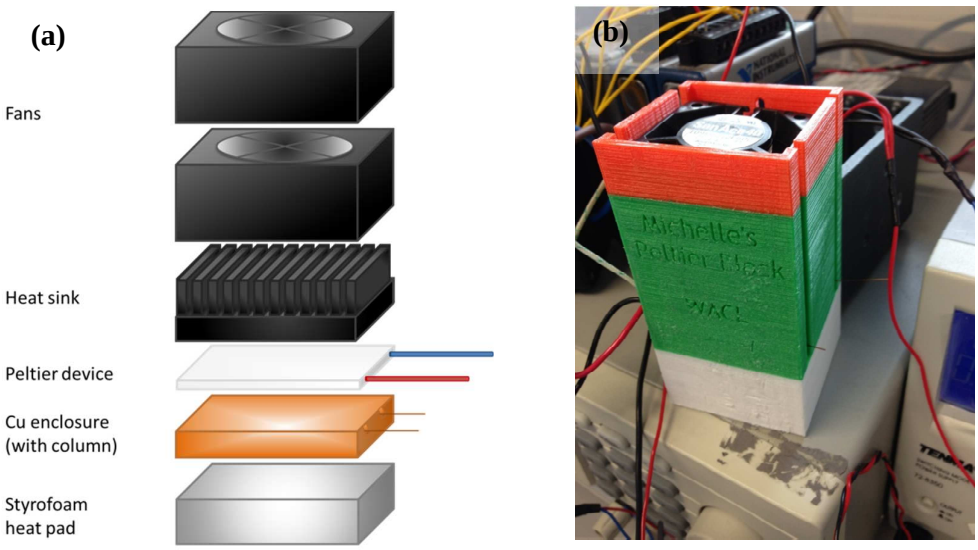


Figure 6-8. (a) Arrangement of the Peltier stack. (b) Peltier stack in a 3D printed block.

6.3 Injection of gaseous sample into GC column

There is a need to find a way to inject samples to the GC column. One way is to use two position valves with a sampling loop, together with a carrier gas flow, to introduce samples to the column. Figure 6-9 shows the concept for this method of injection [177].

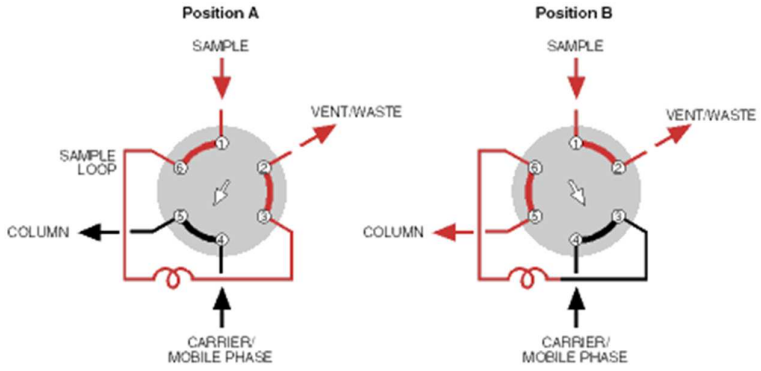


Figure 6-9. Sample injection for a two-position valve.

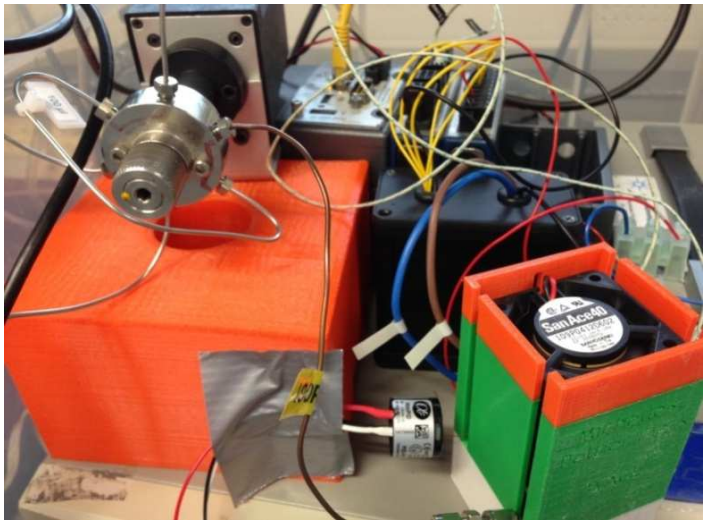


Figure 6-10. Set up of Peltier stack with a two-position valve.

Another method to introduce gas samples is to have a Swagelok fitting together with an airtight septum for needle injection of gas samples. In this case, gaseous samples were picked up at the headspace of a PTFE septum-sealed, screw-thread vial with a gas-tight syringe, and then injected into the septum-sealed Swagelok fitting carrying the air flow into the GC column (as shown in Figure 6-11).

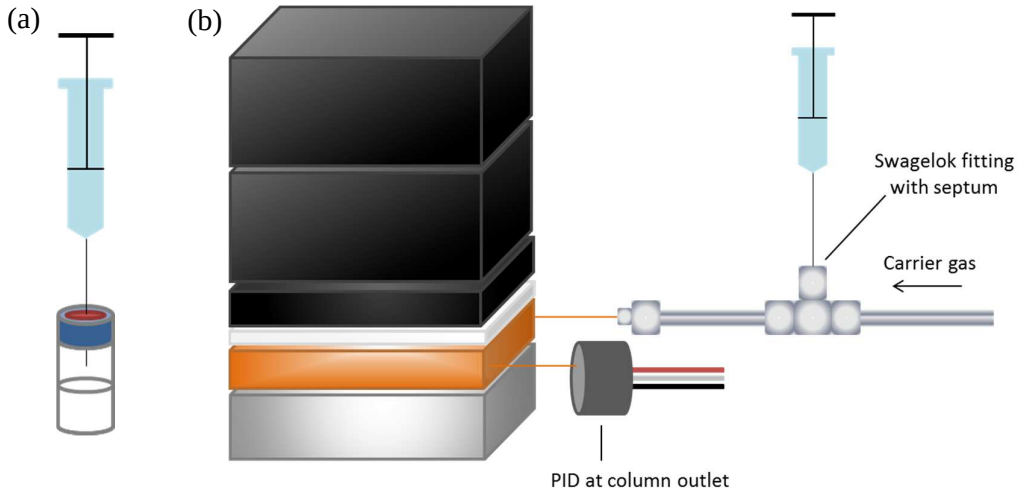


Figure 6-11. (a) Headspace of standards were drawn up by a syringe. (b) Schematic set-up for headspace injection of standards into GC column.

6.4 Detection of gaseous samples with PID

200 µL of neat isoprene (Acros Organics, 98%) and 400 µL of neat toluene (Sigma-Aldrich >= 99.3 %) were pipetted into a screw-thread vial and capped with a septa-sealed cap. 4 µL of the gaseous sample were picked up at the headspace and injected into the Swagelok fitting carrying nitrogen gas flow. The Peltier temperature control was set to 20°C initially, and ramped up at a rate of 10 °C min^{-1} to 80 °C and held for 100 seconds. The outlet nitrogen flow was at 2 mL min^{-1}. The PID used is a low-cost (~200 USD), commercially available PID (PID-AH, Alphasense). The ultraviolet lamp of the PID provided 10.6 eV for

compound ionisation and the device was used as supplied, with the exception of the deliberate removal of a filter inlet placed over the detection grids.

From Figure 6-12, it was observed that the isoprene and toluene peaks were observed under a minute. It was observed that the isoprene peak was more distinct than that of toluene although the ionisation potential of isoprene and toluene are comparable (isoprene: 8.85 eV I.P.; toluene: 8.82 eV I.P.). It was inferred that the lower peak of toluene observed was due to the lower vapour pressure of toluene compared to isoprene (vapour pressure of toluene at 20°C = 0.425 psi; vapour pressure of isoprene at 20°C = 8.82 psi).

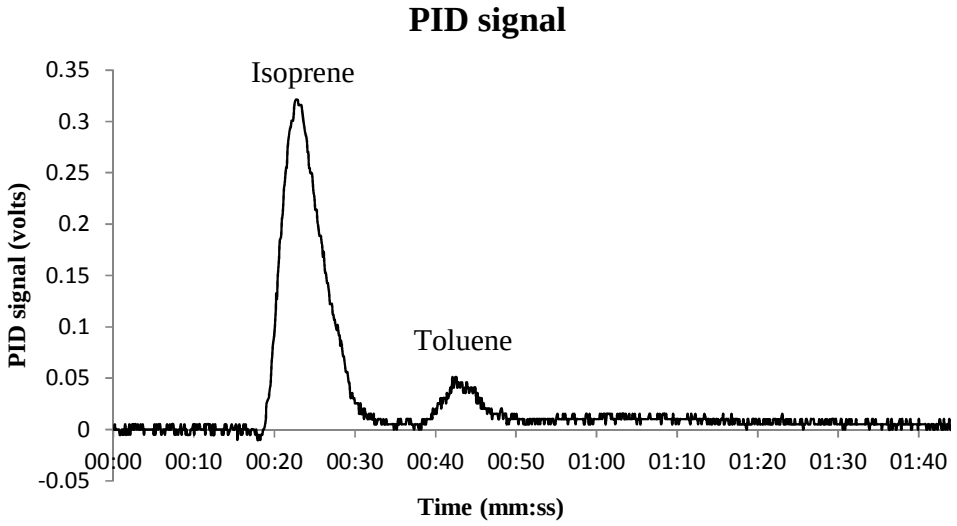


Figure 6-12. PID chromatograph of isoprene and toluene mixture from GC separation with Peltier device. Carrier gas: N_2.

To further test the efficiency of the separation of compounds on the GC followed by their detection on the PID, another compound was added to the mixture. Ethylbenzene (Fluka, analytical standard) was the third compound chosen as it has a reasonable ionisation potential of 8.77 eV. However, as its vapour pressure (0.193 psi at 20 °C) is lower than both isoprene and toluene, 600 µL of neat

ethylbenzene was added to the vial containing 200 µL of isoprene and 400 µL of toluene.

Figure 6-13 shows the PID chromatograph obtained under the same flow, injection and Peltier device conditions. The peak for ethylbenzene was not well-resolved and was observed to be spread across an elution time of about 1 minute.

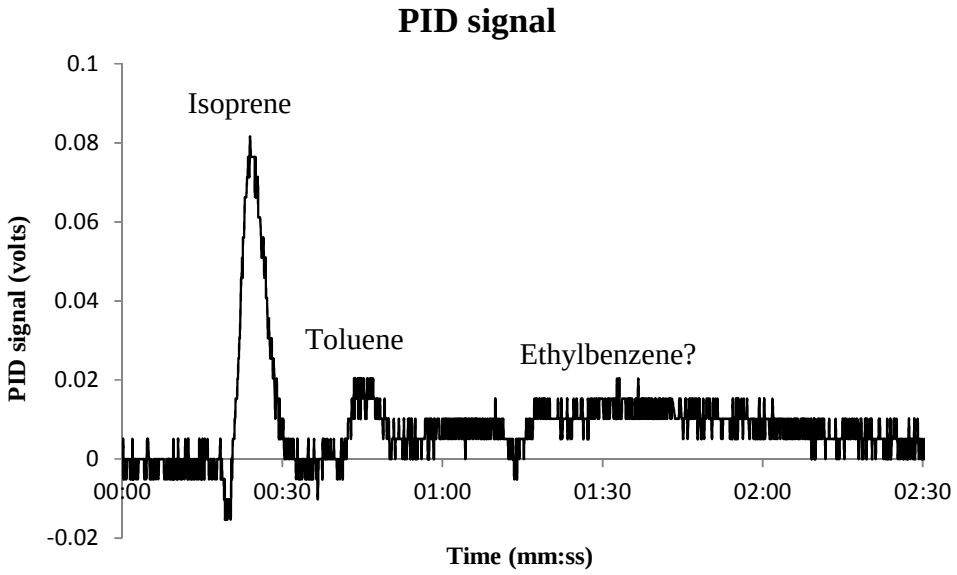


Figure 6-13. PID chromatograph of mixture containing isoprene, toluene and ethylbenzene from GC separation with Peltier device.Carrier gas: N_2.

Due to the nature of the set-up, the flow through the column is operated at a constant head pressure instead of a constant flow rate. The column head pressure is adjusted at room temperature to give an outlet flow rate of 2 mL min^{-1} and this pressure remains constant throughout the analysis. The viscosity of a carrier gas is dependent on temperature; as temperature increases, the viscosity of the carrier gas will increase. In other words, the linear velocity of the carrier gas is subjected to changes when the temperature changes (according to the Peltier device temperature control). Hence, when using the Peltier device to ramp up the

temperature of the column, the viscosity of the carrier gas increases and the average linear velocity decreases.

The average linear velocity of the carrier gas has an impact on the efficiency of the chromatographic set-up. This effect is illustrated with a van Deemter curve as shown in Figure 6-14 [178].

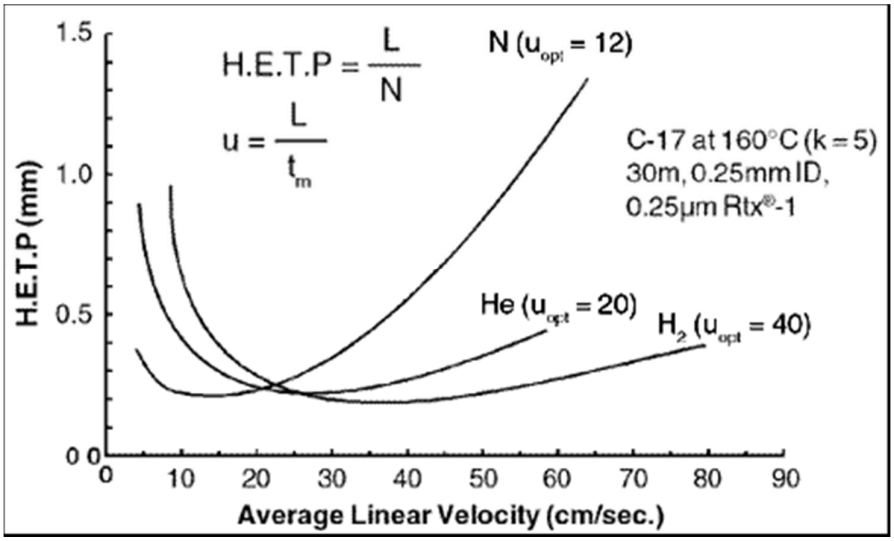


Figure 6-14. Van Deemter plot for nitrogen, helium and hydrogen.

The van Deemter curve plots efficiencies for a range of average linear velocities. The minimum points of the curves indicate the average linear velocities that result in the maximum efficiencies for the different carrier gases. As seen from the curves, nitrogen has an optimum average linear velocity that gives the best efficiency; however, this optimum average linear velocity is comparably much lower than the other two gases. The curve for nitrogen is also much steeper, and a slight change in the velocity will result in a large decrease in efficiency. The sensitivity of nitrogen to the changes in average linear velocity makes it a less ideal carrier gas of choice. With the column dimensions and outlet flow rate of 2 mL min^{-1} used in the set-up, it was calculated that the average linear velocity of

nitrogen was about 86 cm sec^{-1}, which corresponds to a chromatographic set-up of very low efficiency. However, if the carrier gas was changed to helium which has a much flatter van Deemter curve, it was calculated that the average linear velocity would be about 84 cm sec^{-1}, which should correspond to a chromatographic set-up of higher efficiency.

100 µL of neat isoprene, 400 µL of neat toluene and 800 µL of neat ethylbenzene were pipetted into a screw-thread vial and capped with a septa-sealed cap. 10 µL of the gaseous sample were picked up at the headspace and injected into the Swagelok fitting carrying helium gas flow. The Peltier temperature control was set to 20 °C initially, and ramped up at a rate of 20 °C min^{-1} to 80 °C and held for 50 seconds. The outlet helium flow was at 2 mL min^{-1}. Figure 6-15 shows the PID chromatograph obtained.

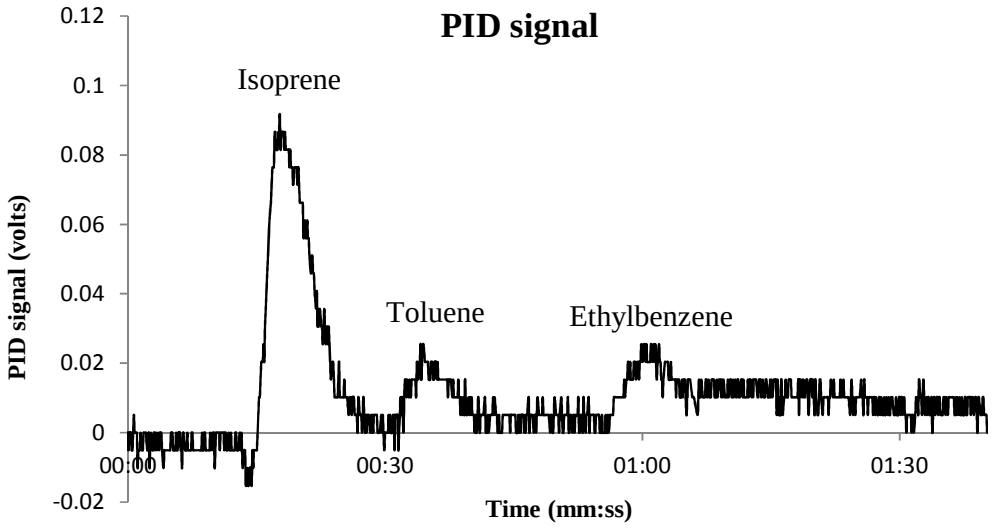


Figure 6-15. PID chromatograph of mixture containing isoprene, toluene and ethylbenzene from GC separation with Peltier device. Carrier gas: He.

It was thought that the lower recovery and less resolved peaks of toluene and ethylbenzene were probably due to losses in the cold transfer lines leading to the

GC column. To minimise losses of the heavier weighted compounds (i.e. toluene and ethylbenzene) due to condensation and deposition on the transfer lines, the lines from the injection point to the inlet of the column were wound with nichrome wire (Pelican Wire Company, 1.70000 Ω) and heated by running a current of about 1.0 A through it. The lines with the nichrome wire were then wrapped with insulation.

50 µL of neat isoprene, 200 µL of neat toluene and 400 µL of neat ethybenzene were pipetted into a screw-thread vial and capped with a septa-sealed cap. 10 µL of the gaseous sample were picked up at the headspace and injected into the Swagelok fitting carrying helium gas flow. The Peltier temperature control was set to 20 °C initially, and ramped up at a rate of 20 °C min^{-1} to 80 °C and held for 50 seconds. The outlet helium flow was at 2 mL min^{-1}. Figure 6-16 shows the PID chromatograph obtained.

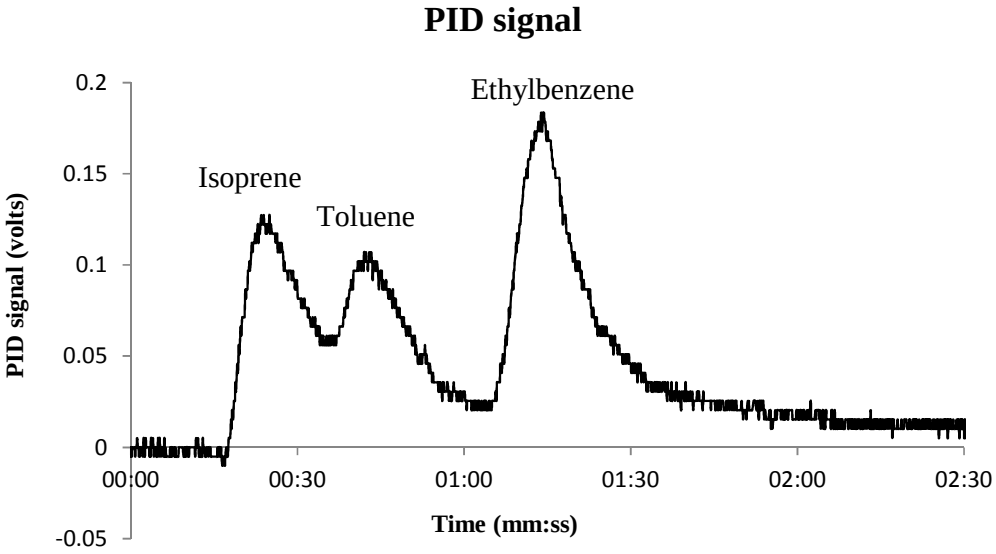


Figure 6-16. PID chromatograph of mixture containing isoprene, toluene and ethylbenzene from GC separation with Peltier device and heated transfer lines. Carrier gas: He.

The heated transfer lines allowed for more of the heavier weighted compounds to be brought into and through the column by reducing their condensation and deposition on the transfer lines. Although there was an increase in the abundance of toluene and isoprene, an overlap in the peaks of isoprene and toluene was also observed.

Another compound, o-xylene, was added to the mixture. 10 µL of the gaseous sample were picked up at the headspace of the vial containing 50 µL of neat isoprene, 200 µL of neat toluene, 400 µL of neat ethylbenzene, and 400 µL of neat o-xylene, and injected into the Swagelok fitting carrying helium gas flow. Figure 6-17 shows the PID chromatograph obtained.

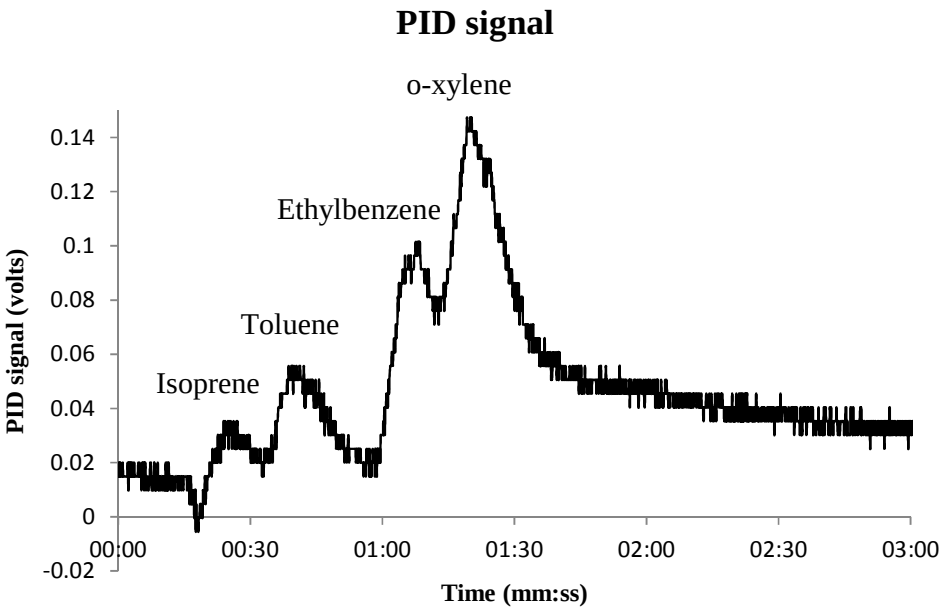


Figure 6-17. PID chromatograph of mixture containing isoprene, toluene, ethylbenzene and o-xylene from GC separation with Peltier device and heated transfer lines. Carrier gas: He.

To demonstrate the importance of having a Peltier temperature control, a series of isothermal runs were carried out. Similar to the experiment carried out previously, 10 µL of the gaseous sample were picked up at the headspace of the vial containing 50 µL of neat isoprene, 200 µL of neat toluene, 400 µL of neat ethylbenzene, and 400 µL of neat o-xylene, and injected into the Swagelok fitting carrying helium gas flow. The isothermal experiments were carried out at 10 ℃, 20 ℃, 30 ℃, 40 ℃, 50 ℃, 60 ℃, 70 ℃ and 80 ℃. Figure 6-18 shows the PID chromatographs obtained for the isothermal experiments.

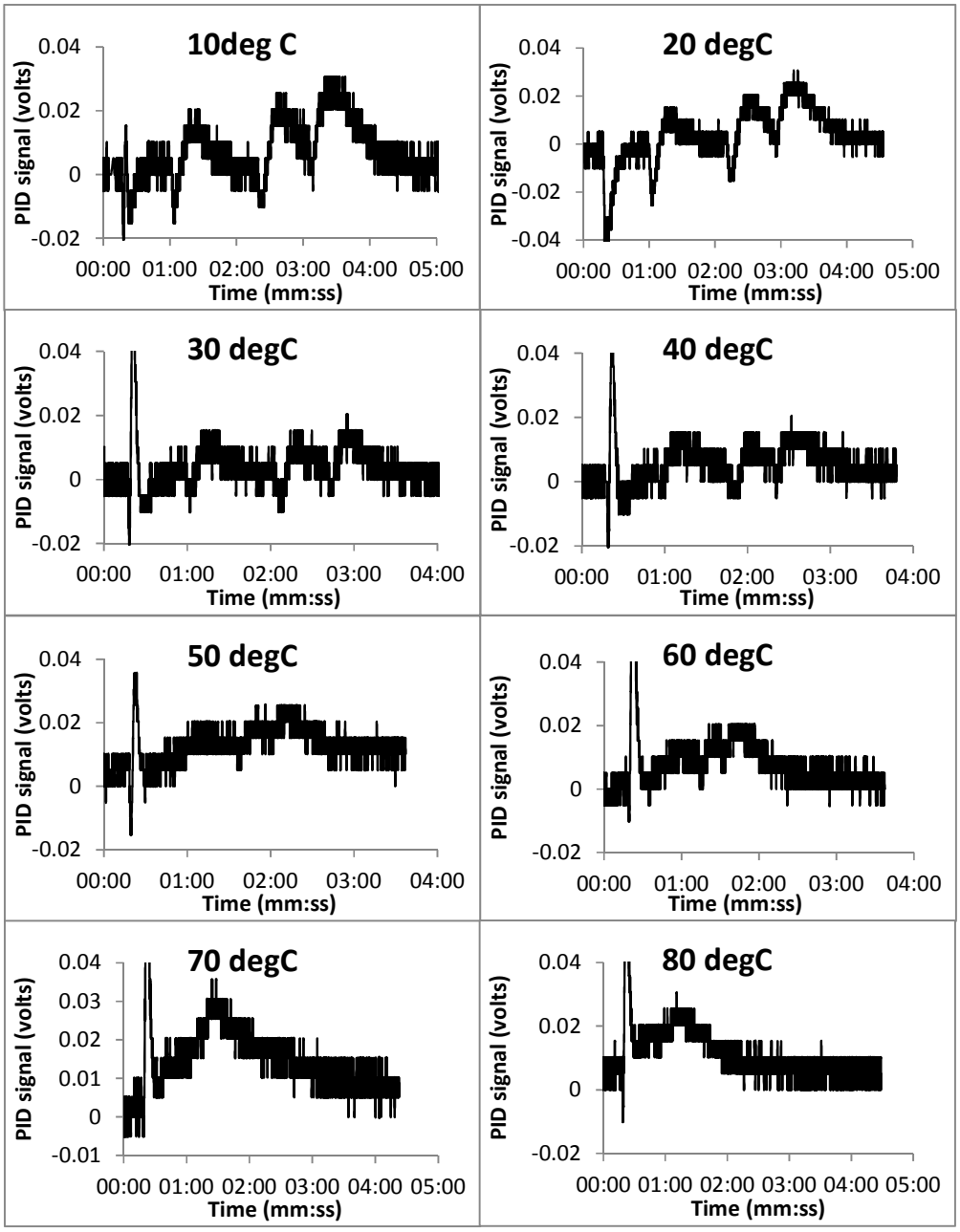


Figure 6-18. PID chromatograph of mixture containing isoprene, toluene, ethylbenzene and o-xylene from GC separation with Peltier device at isothermal temperatures and heated transfer lines. Carrier gas: He.

Evident from the isothermal experiments, there was no good separation between the compounds when temperature was held constant. It was observed the lower the isothermal temperature, the longer it took for all the compounds to be eluted from the column (i.e. about 4 minutes for temperature held at 10 °C, and about 3 minutes for temperature held at 40 °C). At lower isothermal temperatures of 10 °C – 40 °C, the four compounds peaks were still vaguely distinct. As the isothermal temperature increased from 50 °C up to 80 °C, the four compound peaks seemed to converge into one broad peak. It was also noted that with higher isothermal temperatures, elution occurred earlier than at lower temperatures. This set of isothermal experiments highlighted the importance of a gradient temperature control for the better separation of compounds. Holding the temperature at a lower initial temperature allows for the earlier eluting compounds to be better speciated from the larger and later eluting compounds. A temperature ramping up from a low initial temperature then allows for the elution of the larger compounds with higher boiling points at a faster rate with less peak broadening. As seen from Figure 6-17, with a temperature gradient control, the separation of the four compounds was distinct and completed within about 2 minutes.

6.5 Future work

The Peltier temperature control and the detection method by the PID have been tested to be successful for their intended functions when integrated together with a short length of wound commercial GC column. With the previous experiments, there was a proof of concept in the making of the miniaturised air quality sensor when tested with known gas standards. However, there is still a substantial amount of work left to be done in the development of a fully functional and portable air quality sensor, especially in the development of a GC LOC chip and in the integration of the different components that make up the sensor.

6.5.1 GC LOC

The making of a functional GC LOC chip has been one of the biggest challenges faced in the making of the sensor. The manufacture of the PDMS chip has met with various issues, such as the fixing of a needle at the inlet and outlet of the chip, and the gas tightness of the PDMS-glass interface. In the previous experiments, a copper enclosure containing a short length of wound commercial GC column was used in place of the initial intended PDMS chip due to these problems faced. Proper inlet and outlet fixtures, as well as the gas tightness between the PDMS-glass interface and at the connection points, would be necessary for further tests to be carried out on the PDMS GC-LOC. It was to be tested if the PDMS material on its own could be a stationary phase for the separation of gaseous compounds in a mixture, and whether it was necessary to coat it with a film of stationary phase. The optimal width and length of the PDMS channels and the flow rate could also be explored after the successful manufacture of a functional chip.

6.5.2 Adsorption-desorption step prior to separation

In the laboratory, gaseous samples are first introduced to a thermal desorption unit prior to separation on a GC column. The gaseous samples are sampled onto a trap packed with sorbent which essentially selectively adsorbs and retains the compounds of interests. The adsorbed compounds are then extracted by heating the trap, and transferred to the GC in the flow of carrier gas. This adsorption-thermal desorption step is essentially a combination of pre-analytical procedures such as sample preparation, selective concentration, and extraction of compounds. For the analysis of real samples which may contain only trace levels of compounds, this step is especially important for the preparation and concentration of the gas samples before they are introduced into the GC system.

A miniaturised format of the thermal desorption unit would be required for the development of a portable air quality sensor. It was thought that a length of porous layer open tubular (PLOT) column could be used as the adsorbent prior to separation by the GC system. The inner surface of a PLOT column is coated with a layer of porous stationary solid phase particles such as alumina or molecular sieves. When gaseous samples pass through the PLOT column, selected compounds will be adsorbed onto the porous stationary phase. To extract the adsorbed compounds, heat will be supplied to the PLOT column to allow for desorption in the flow of a carrier gas.

A simple concept could be used for the thermal desorption of compounds from the PLOT column. It was thought that the PLOT column could be coated with a silver-based electricity-conducting ink. To heat up the short length of column, a voltage could be supplied to the PLOT column that has been coated with the ink. Heat generated from the conductivity is expected to be high enough to allow for the fast desorption of compounds in an acceptably small plug of vapour. Figure

6-19 shows the schematic of a PLOT column that is coated with electricity-conductivity ink.

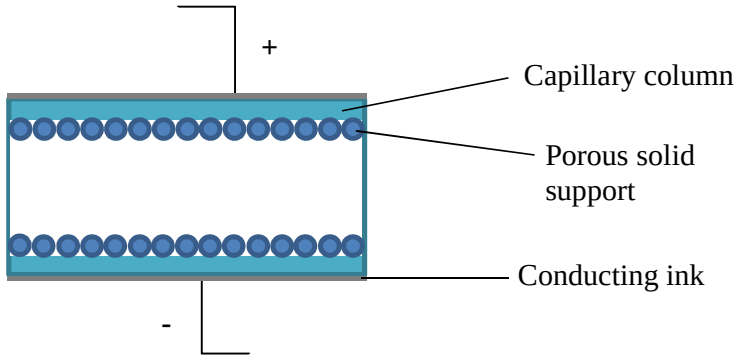


Figure 6-19. Schematic of a conducting-ink coated PLOT column for adsorption-thermal desorption.

6.5.3 Integration of parts that make up the sensor

It is crucial for the successful integration of the different components that make up the sensor device, i.e. the carrier gas supply, introduction/injection of samples, thermal desorption component, the GC LOC, the Peltier temperature control device, and the PID as the detection means. Rigorous testing has to be conducted on each component itself to ensure its feasibility before it can be coupled with other parts for further testing. The integration of the different components is often challenging – the integrity of the gas samples has to be maintained with no leakage, while at the same time ensuring that the intended function of each component is still being carried out at the right time.

The system has to be properly packaged into a portable unit together with the power supply units and data analysis unit (typically a laptop). As this point, we have the Peltier device together with the heat sink and fans, and the copper enclosure with the GC column packaged together in a “Peltier stack” (see Figure 6-8b). This was made with a 3D printer that allowed for the customisation of the

exact dimensions required. When the prototype of a functional system has been made, a customised 3D-printed storage could be made to contain the different components of the sensor device.

Appendix A

Chromatograms and mass spectra for indoor air analysis

Home 01

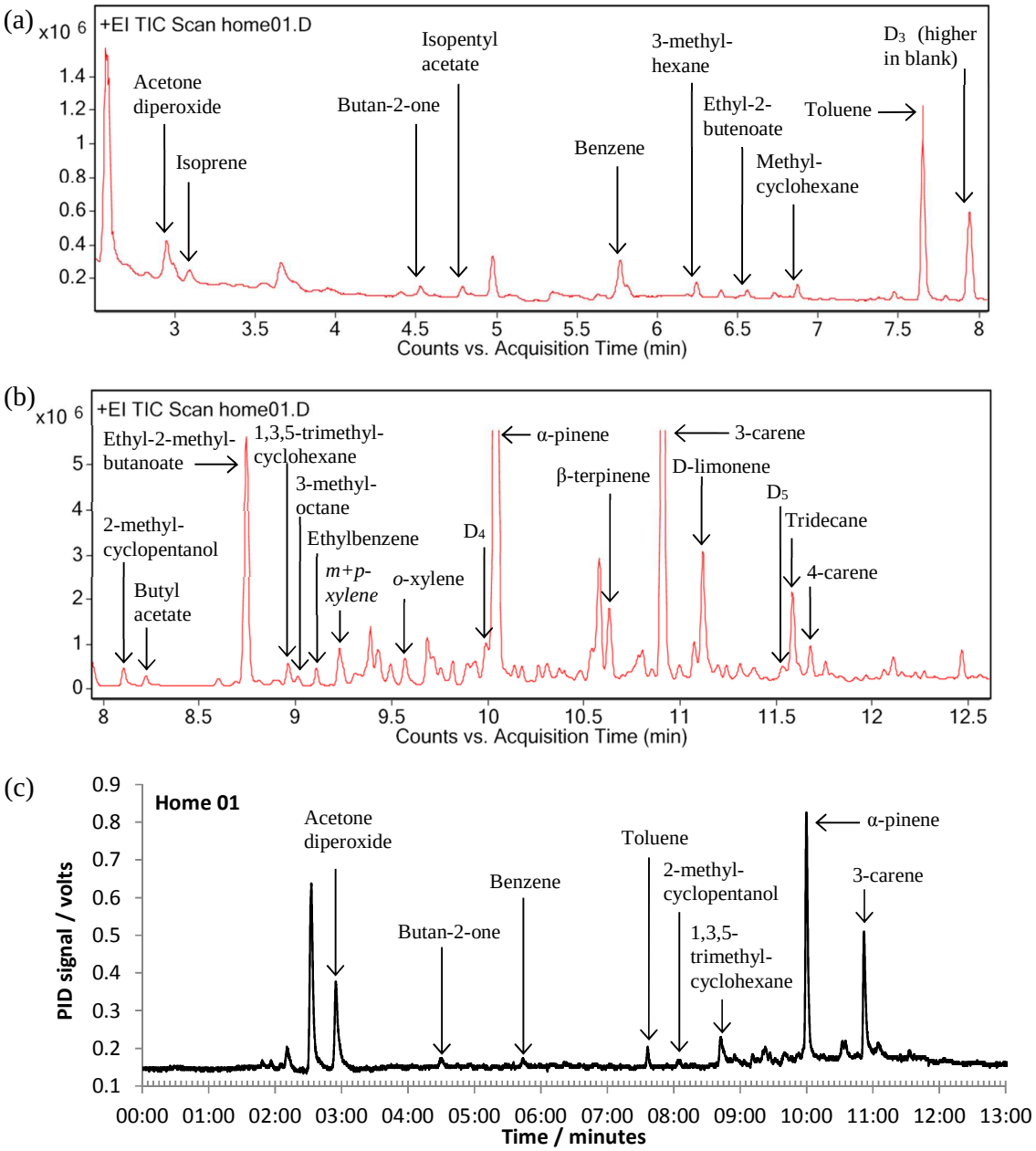


Figure A-1. Analysis of Home 01: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 12.5 min and (c) detection by PID.

Home 02

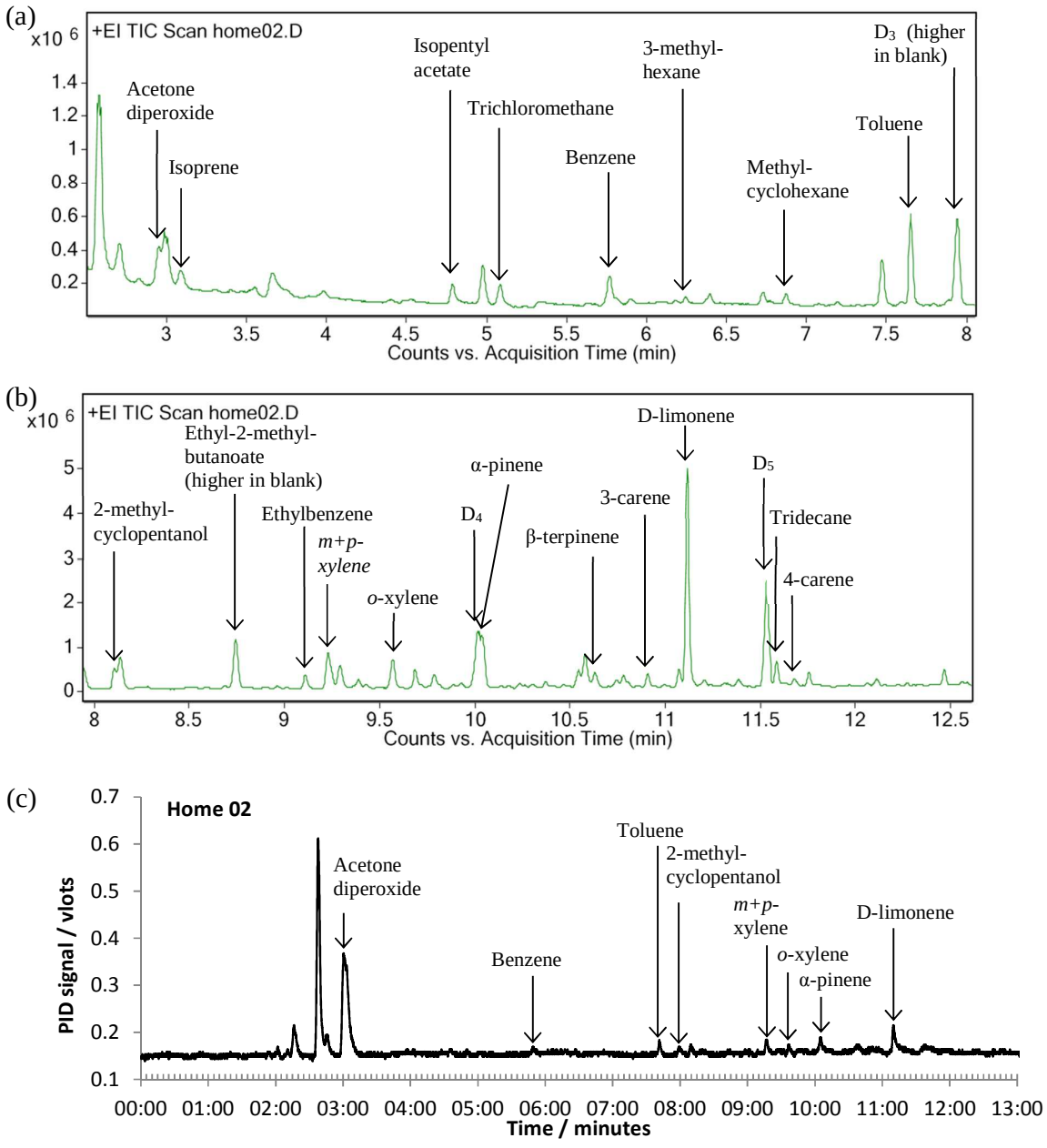


Figure A-2. Analysis of Home 02: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 12.5 min and (c) detection by PID.

Home 03

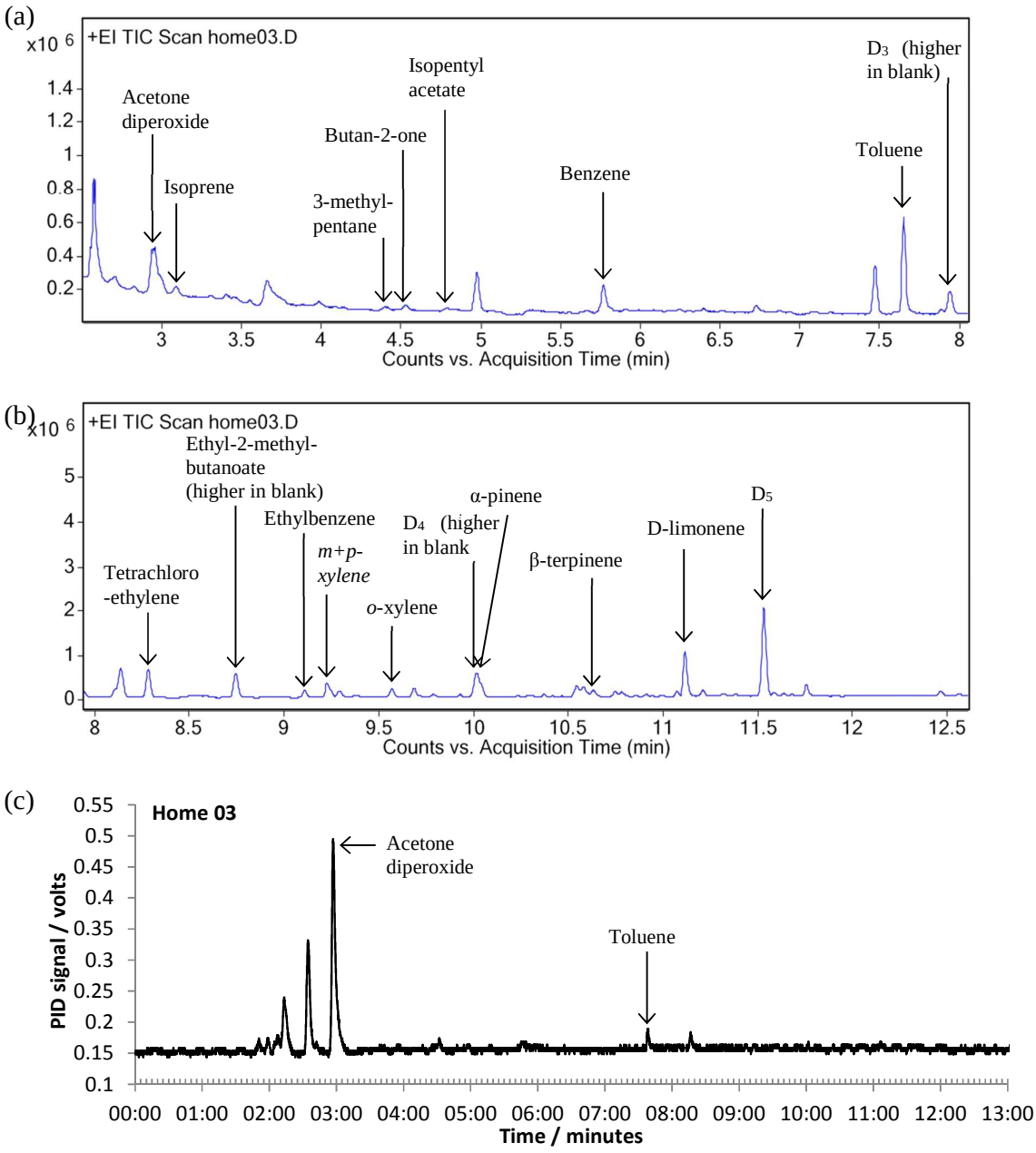


Figure A-3. Analysis of Home 03: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 12.5 min and (c) detection by PID.

Home 04

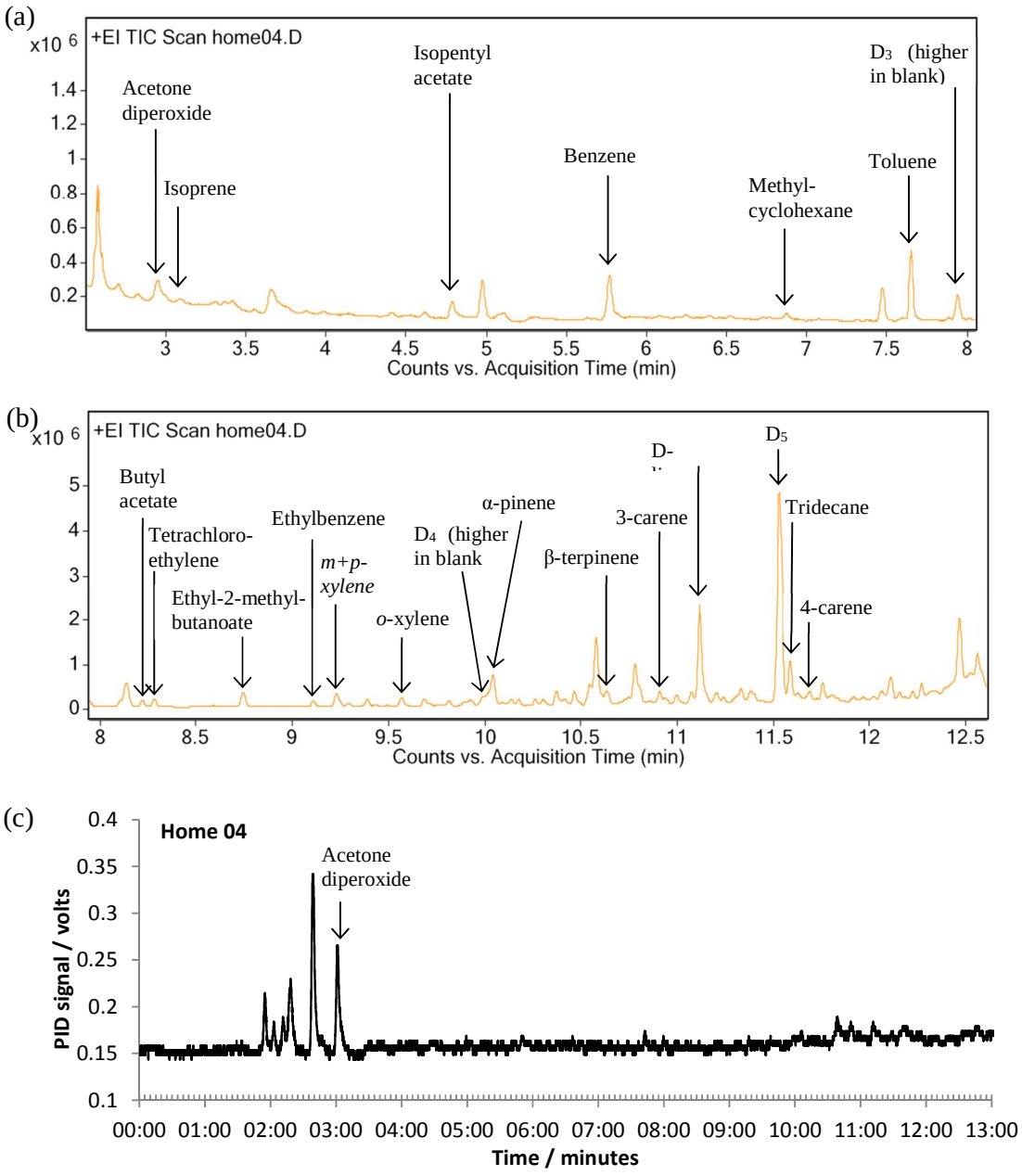


Figure A-4. Analysis of Home 04: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 12.5 min and (c) detection by PID.

Home 05

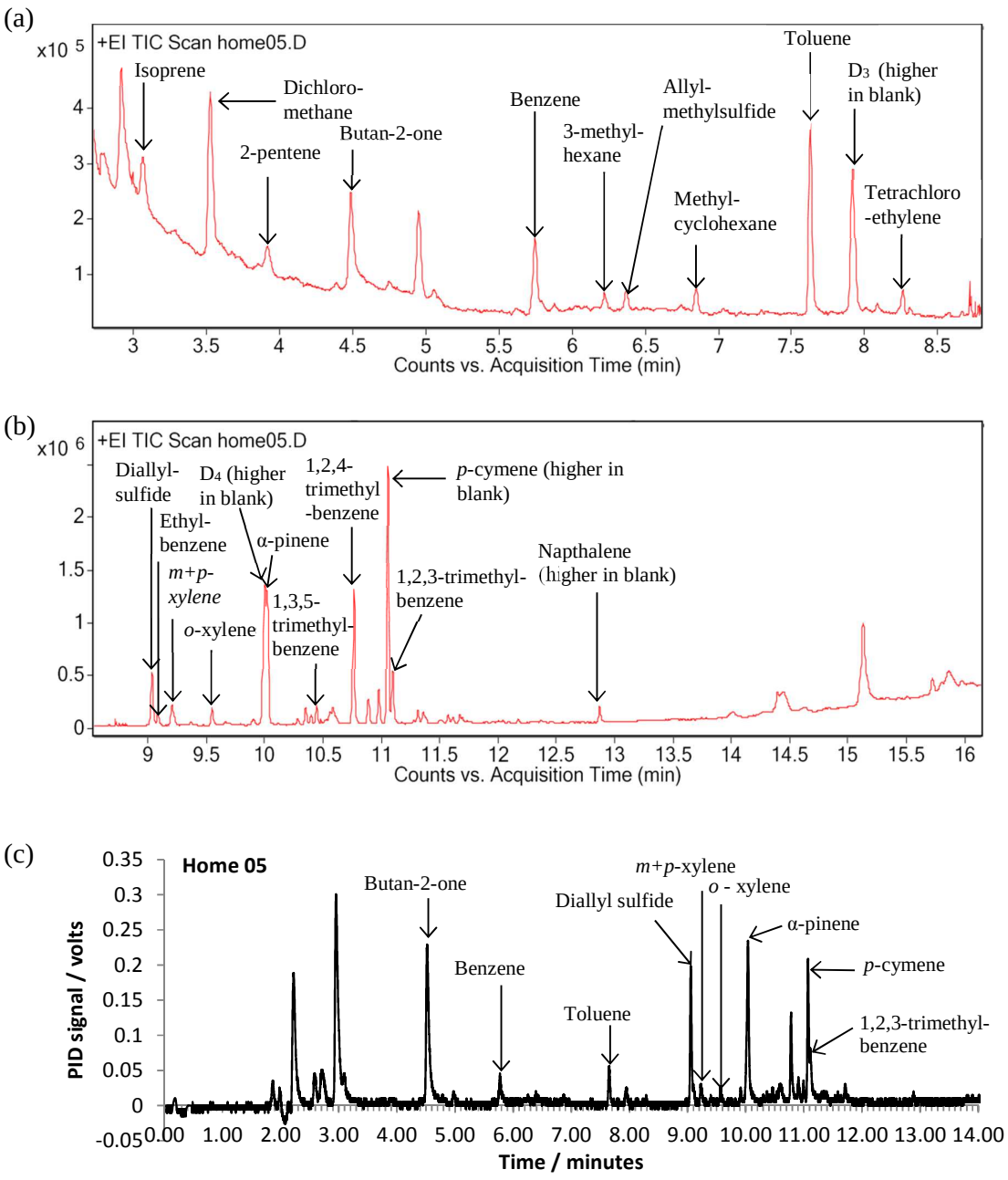


Figure A-5. Analysis of Home 05: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 16 min and (c) detection by PID.

Home 06

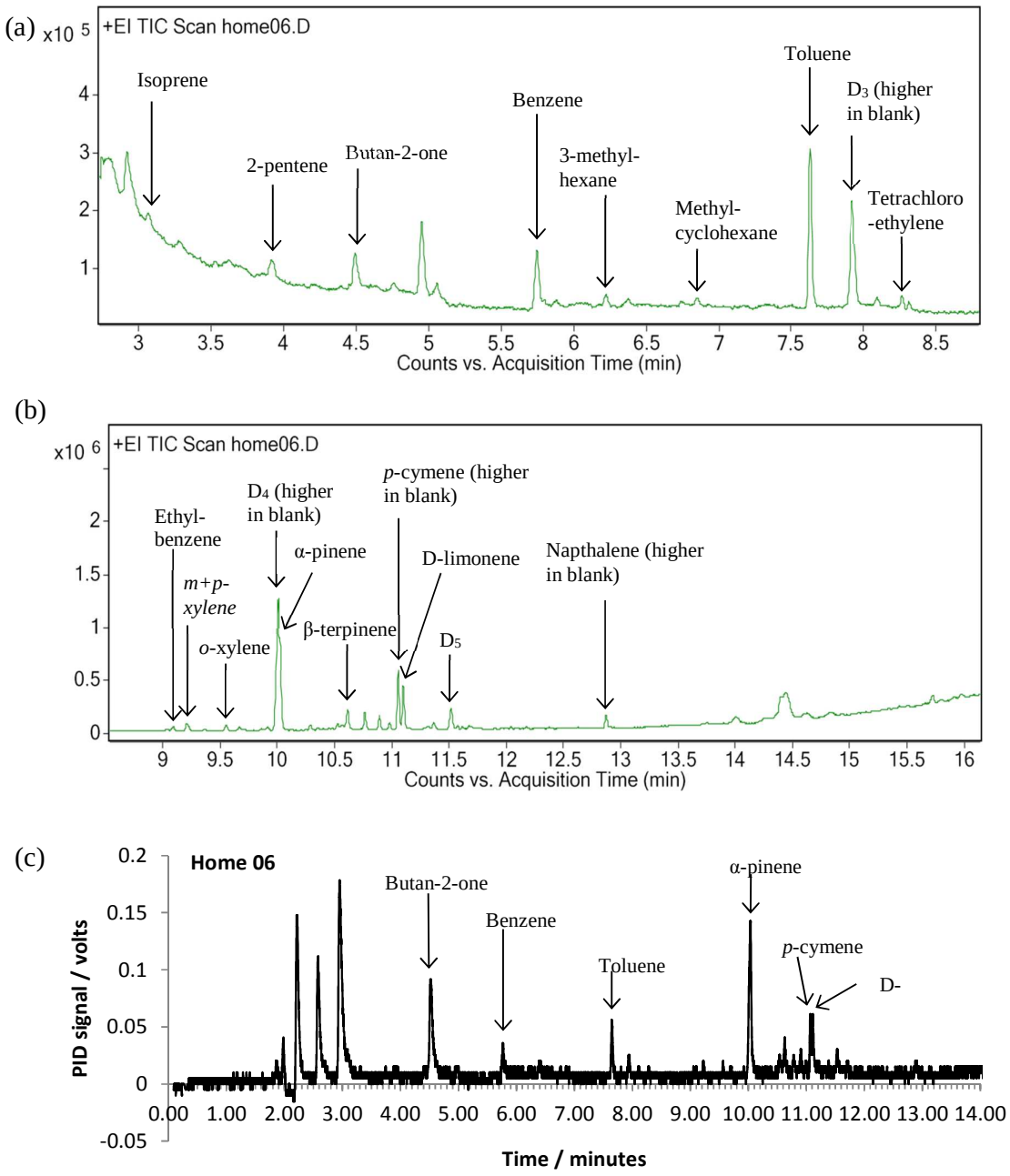


Figure A-6. Analysis of Home 06: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 16 min and (c) detection by PID.

Home 07

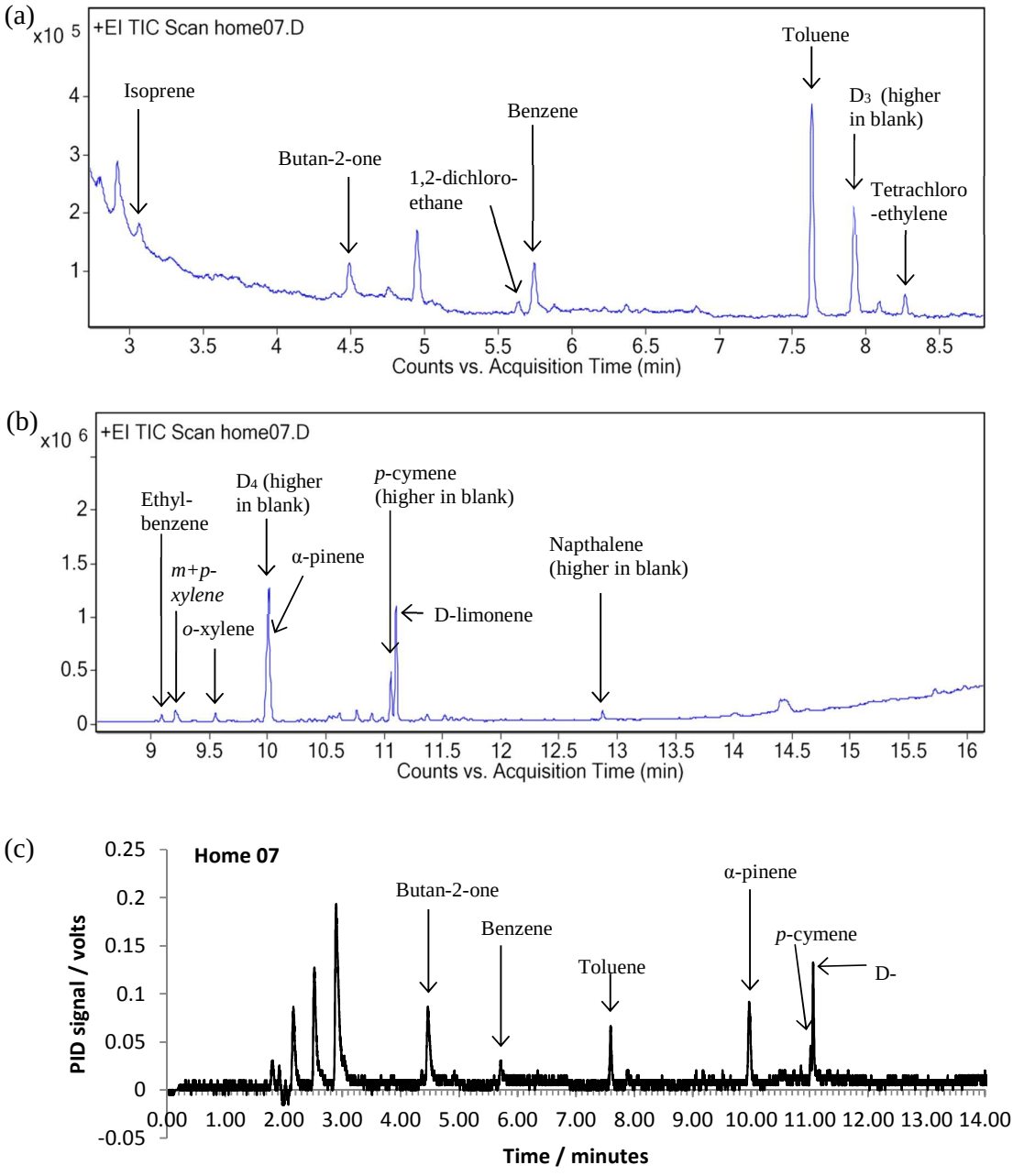


Figure A-7 Analysis of Home 07: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 16 min and (c) detection by PID.

Home 08

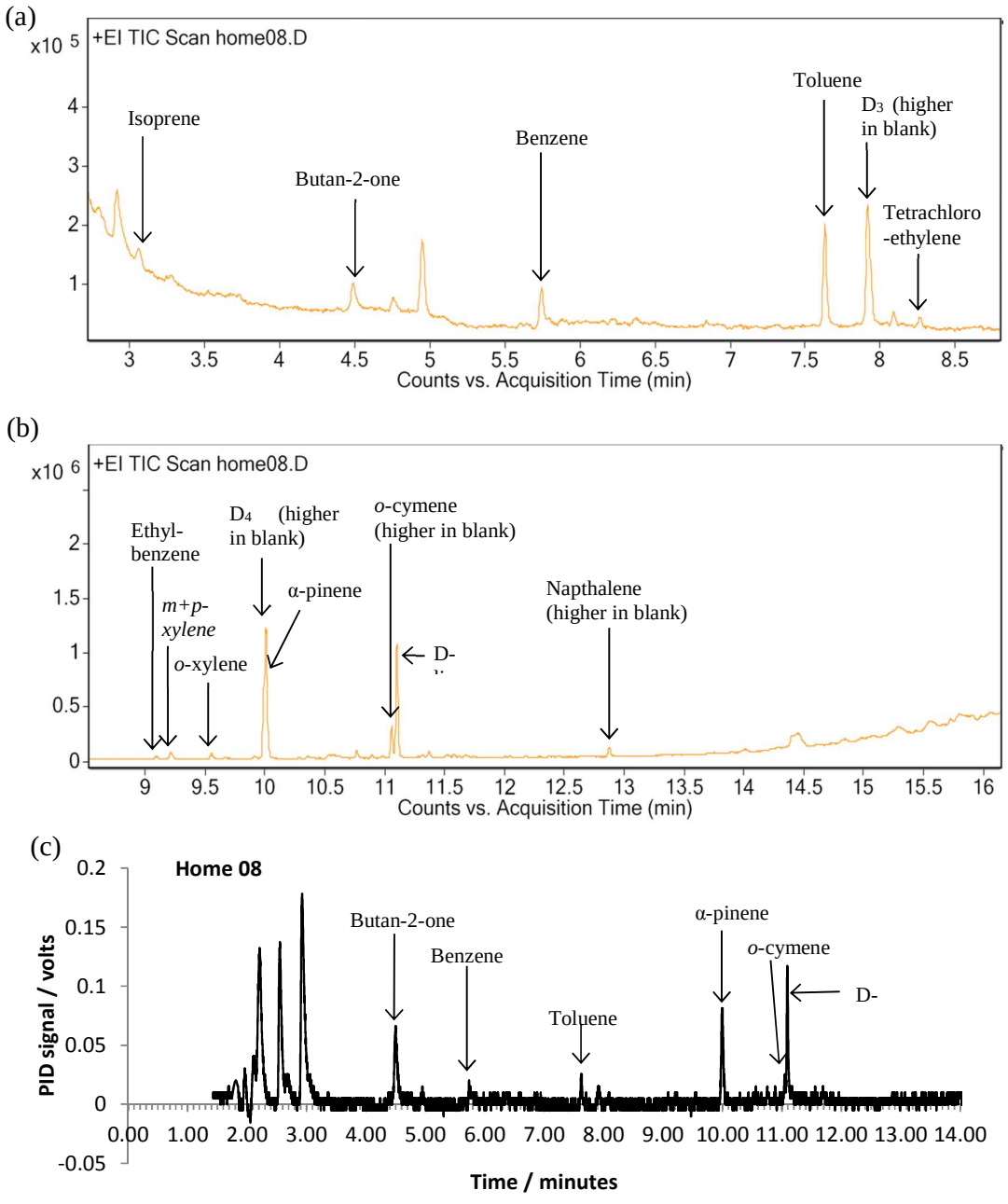


Figure A-8. Analysis of Home 08: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 16 min and (c) detection by PID.

Home 09

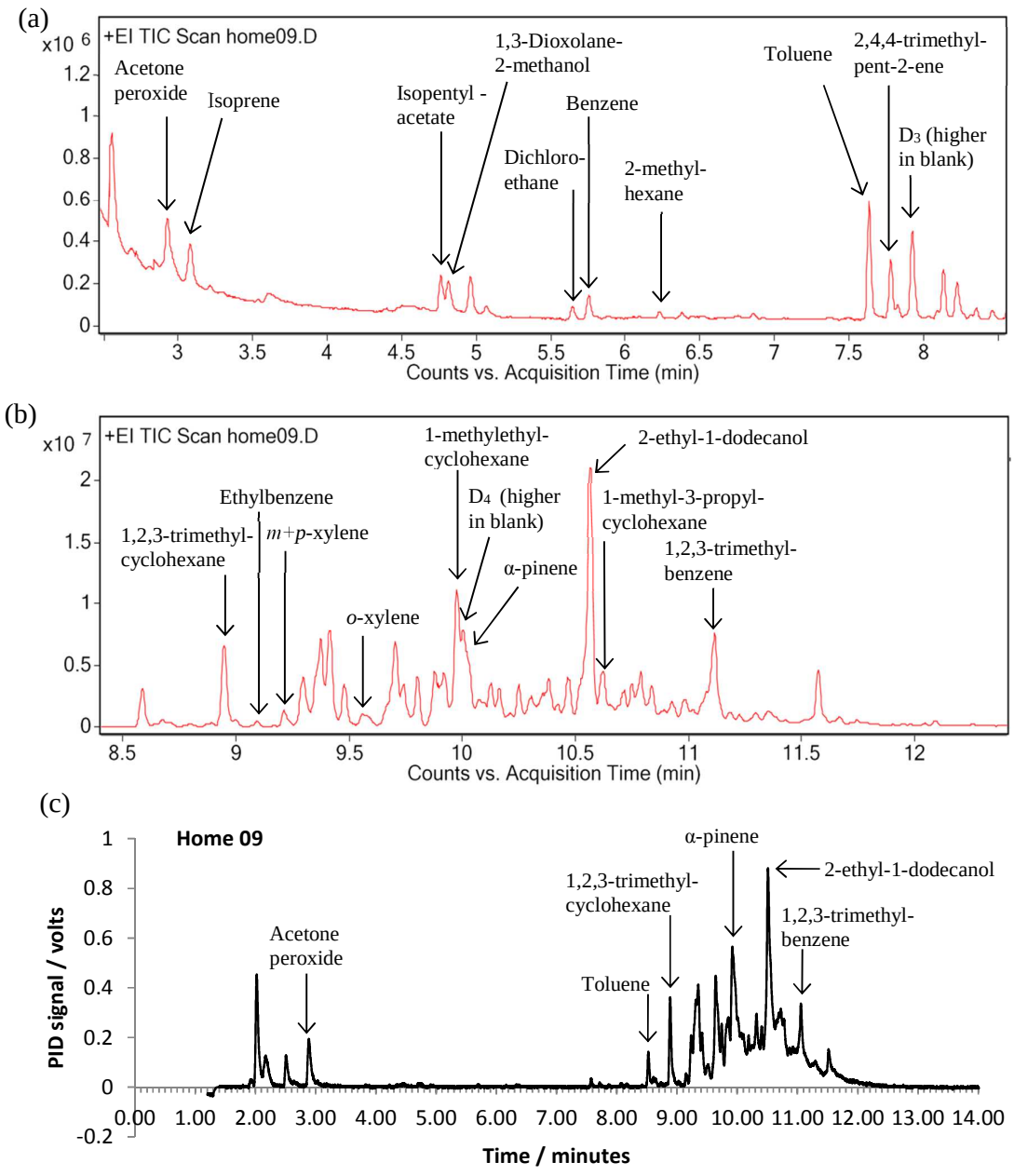


Figure A-9. Analysis of Home 09: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 12.5 min and (c) detection by PID.

Home 10

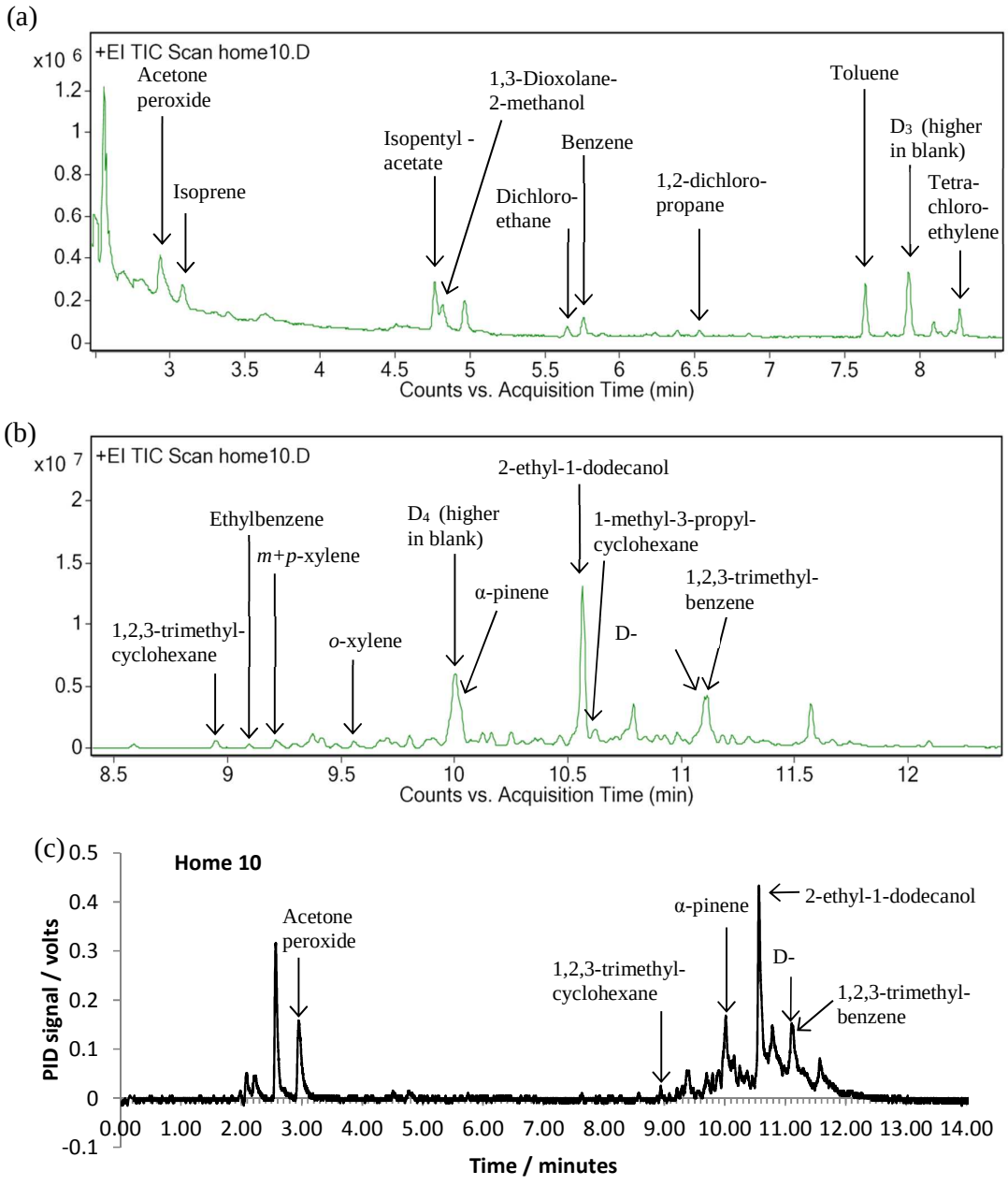


Figure A-10. Analysis of Home 10: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 12.5 min and (c) detection by PID.

Home 11

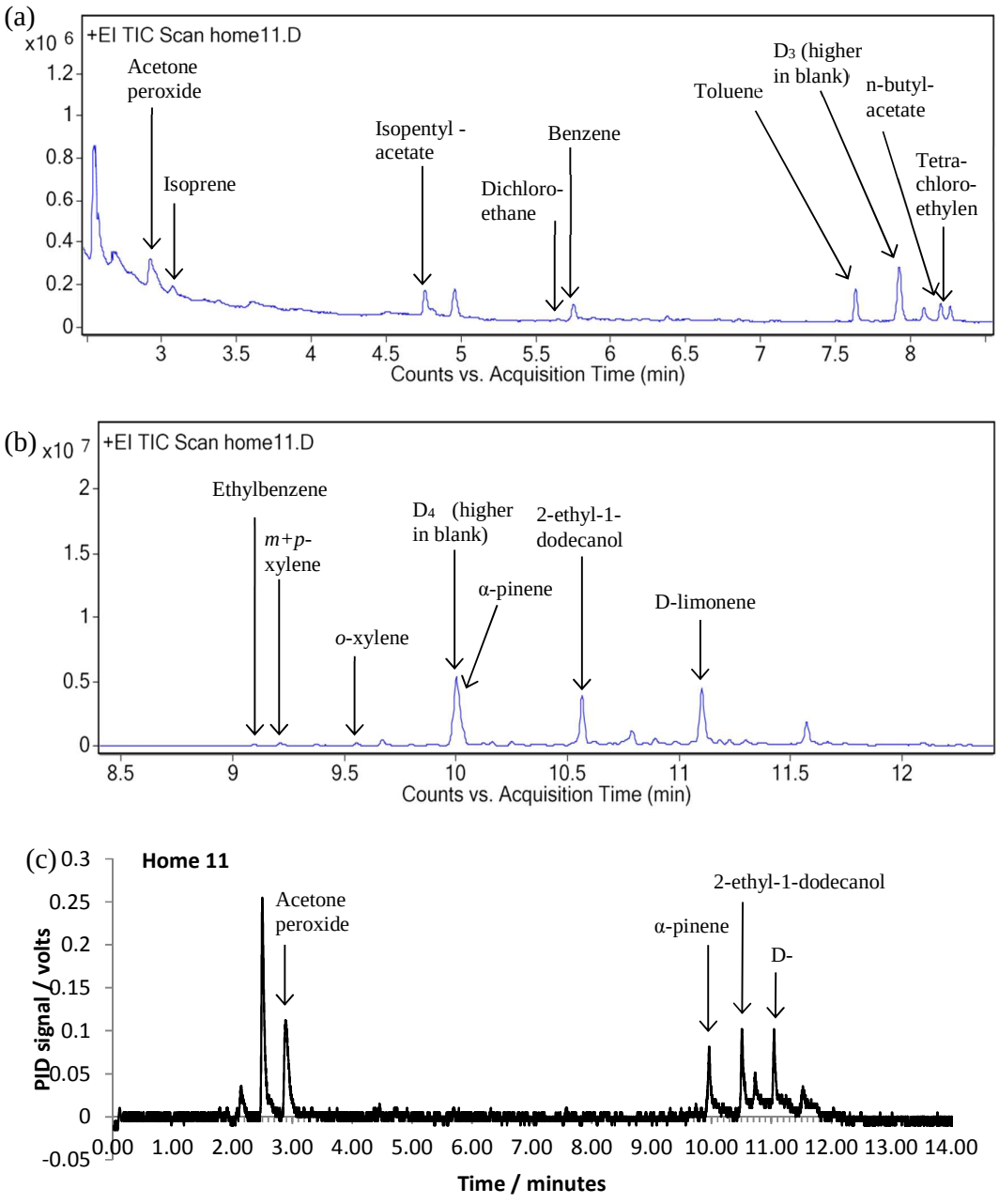


Figure A-11. Analysis of Home 11: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 12.5 min and (c) detection by PID.

Home 12

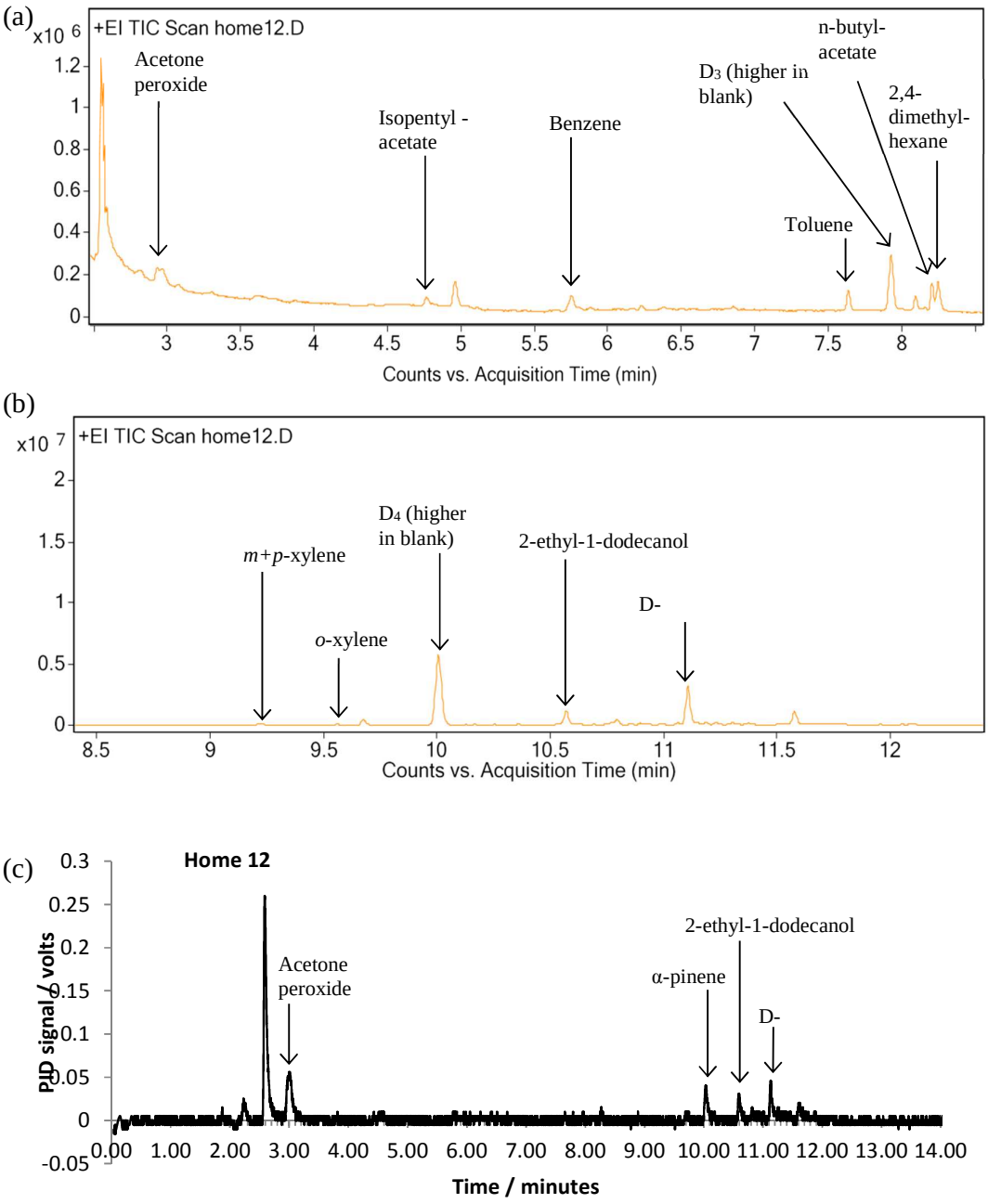


Figure A-12. Analysis of Home 12: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 12.5 min and (c) detection by PID.

Home 13

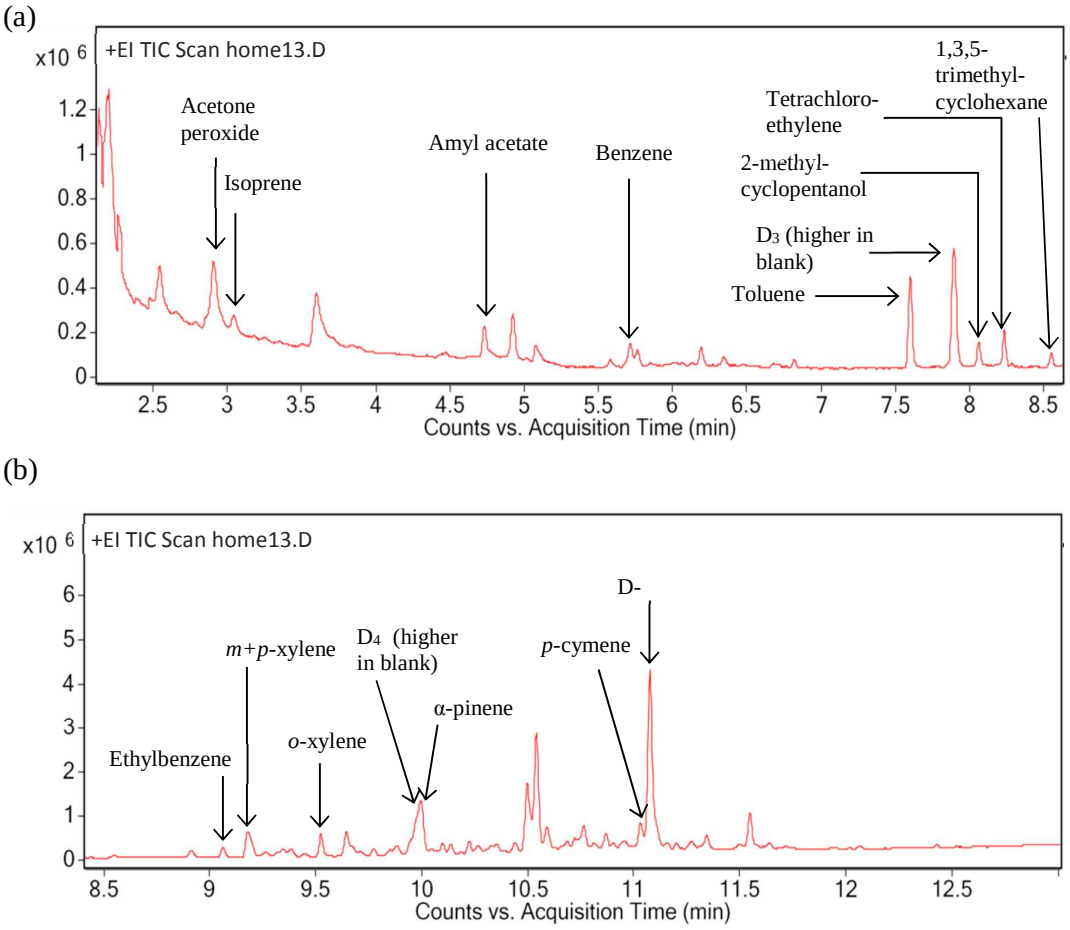


Figure A-13. Analysis of Home 13: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 13 min.

Home 14

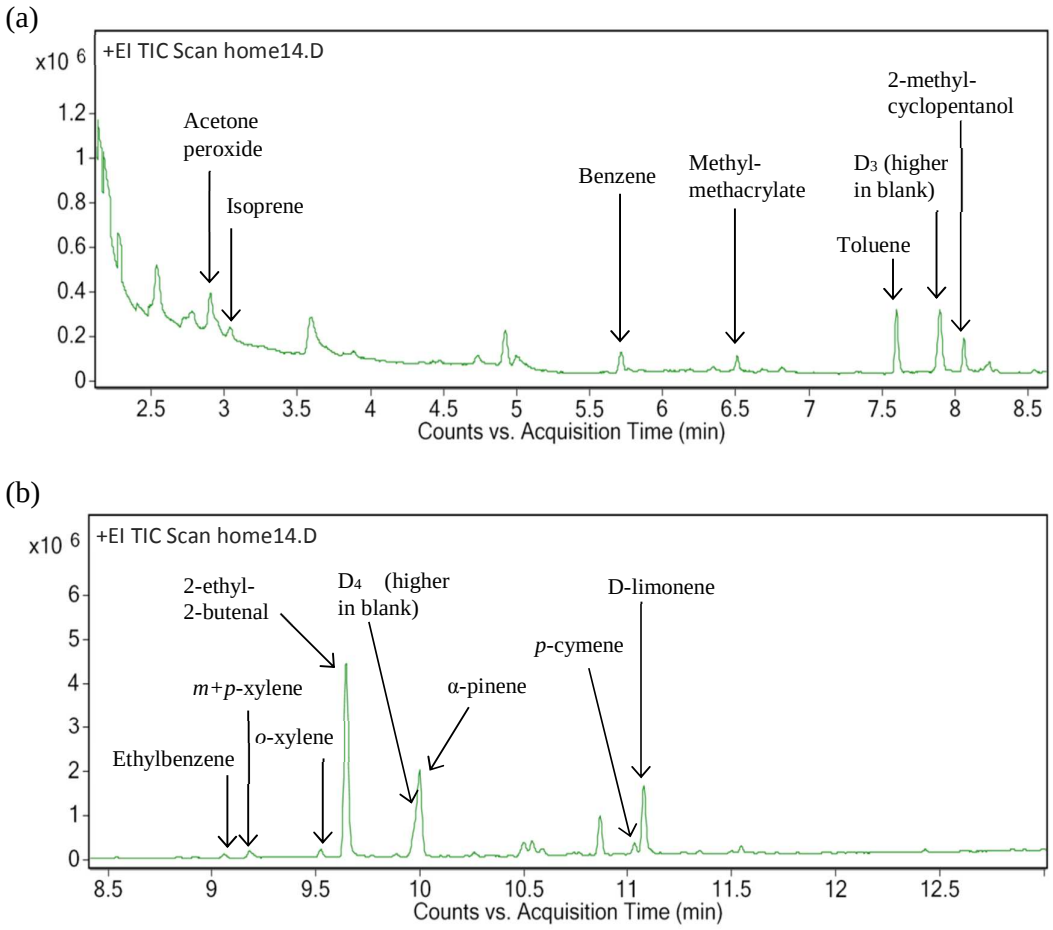


Figure A-14. Analysis of Home 14: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 13 min.

Home 15

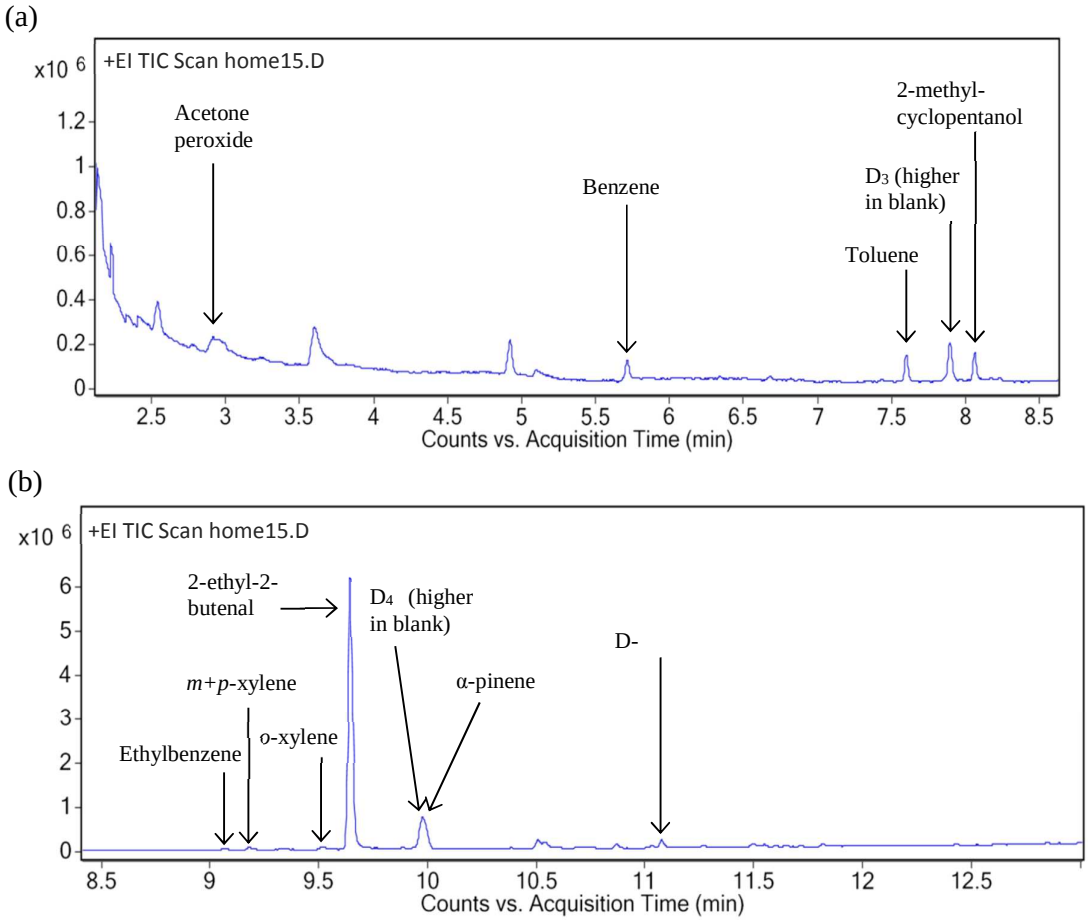


Figure A-15. Analysis of Home 15: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 13 min.

Home 16

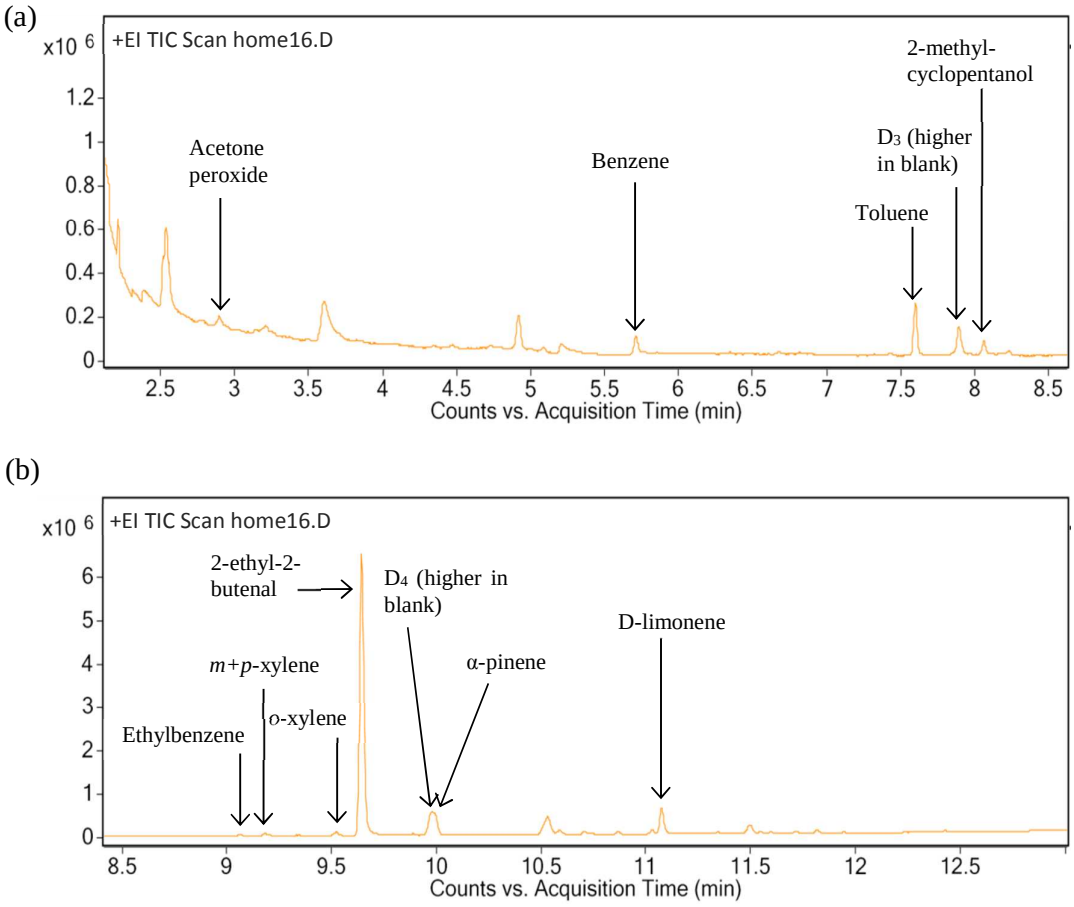


Figure A-16. Analysis of Home 16: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8.5 min and (b) 8.5 – 13 min.

Home 17

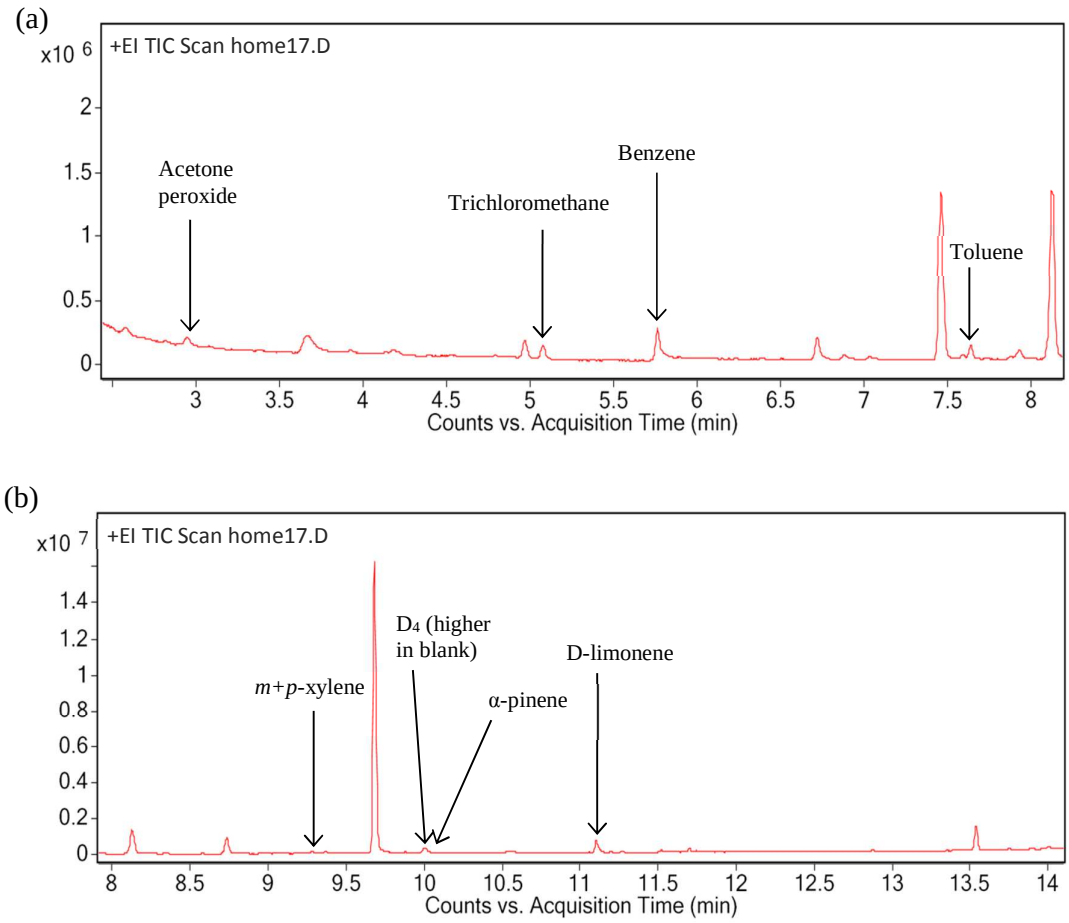


Figure A-17. Analysis of Home 17: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 14 min.

Home 18

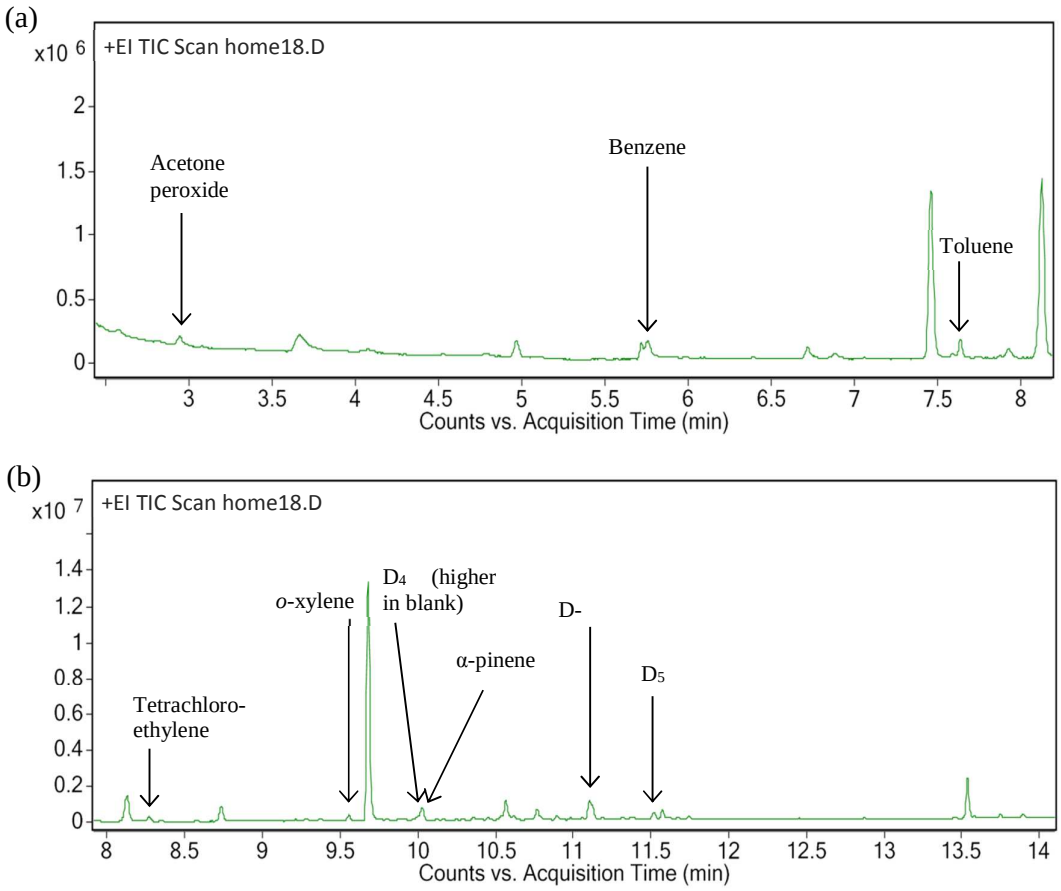


Figure A-18. Analysis of Home 18: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 14 min.

Home 19

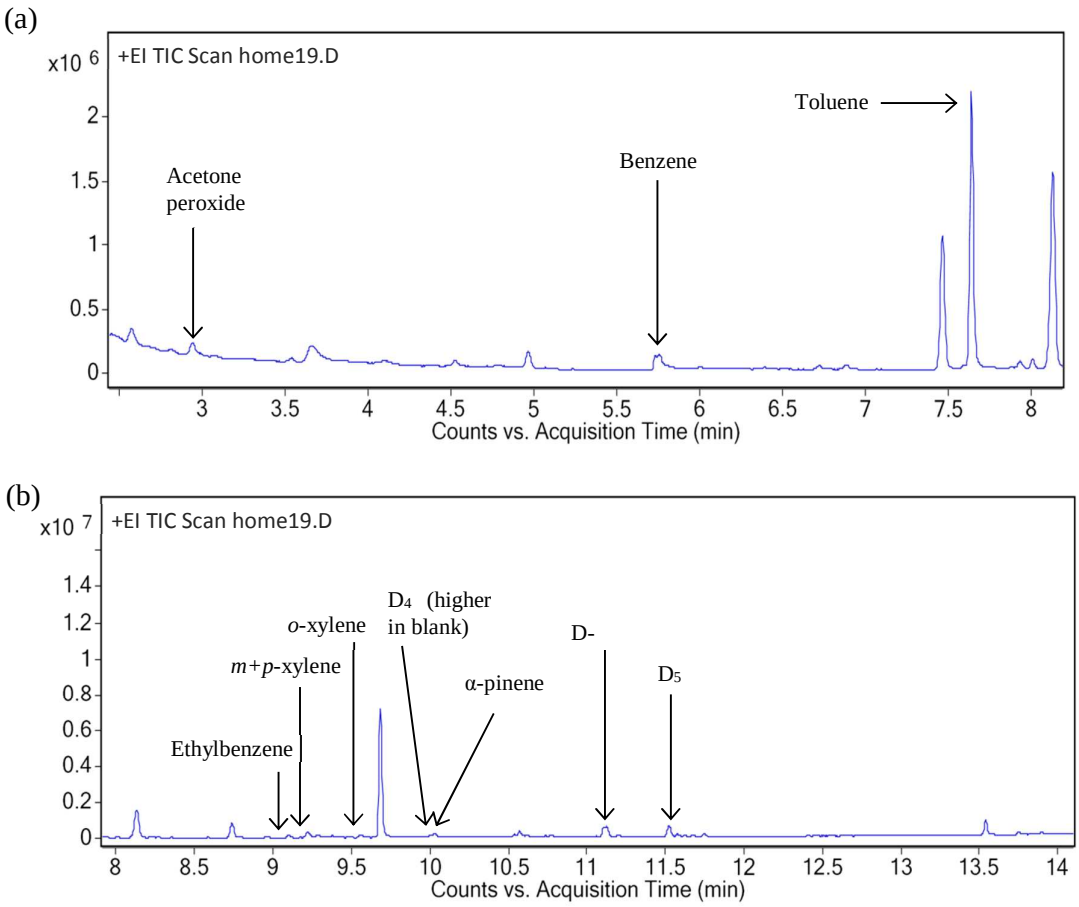


Figure A-19. Analysis of Home 19: Detection by laboratory standard TOF/MS detector (a) from 2.5 – 8 min and (b) 8 – 14 min.

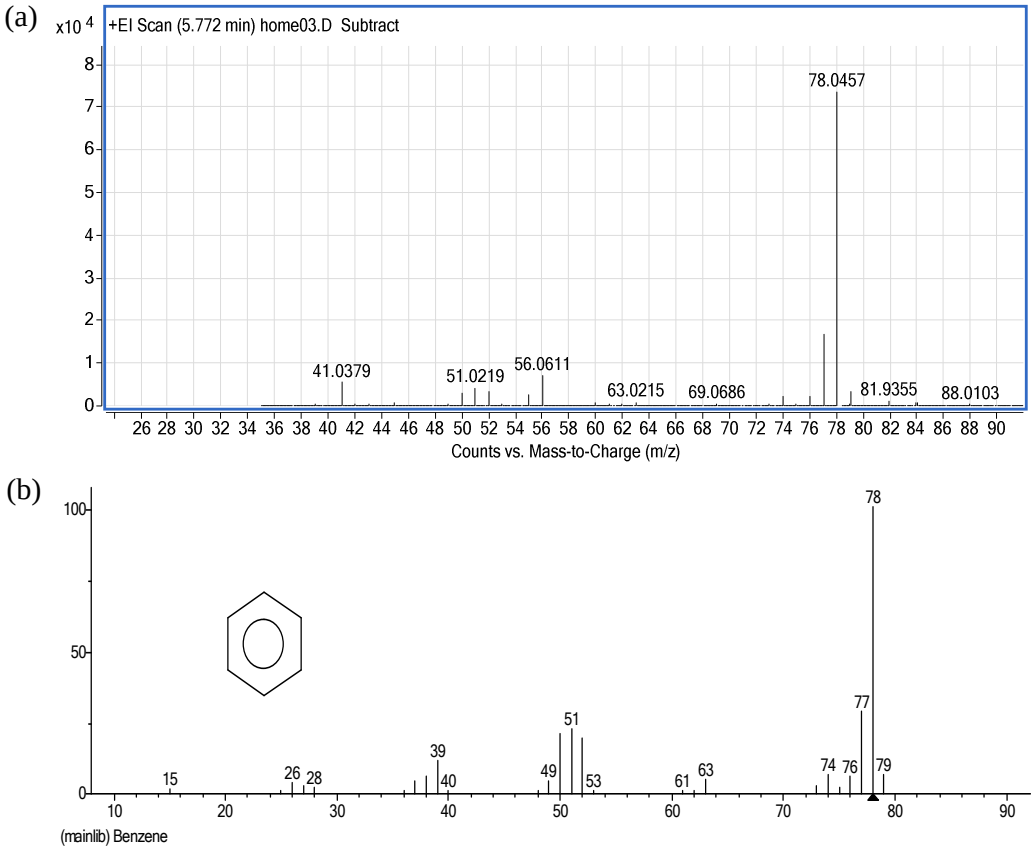


Figure A-20. Mass spectra of benzene (a) from Home 03 and (b) from NIST MS library.

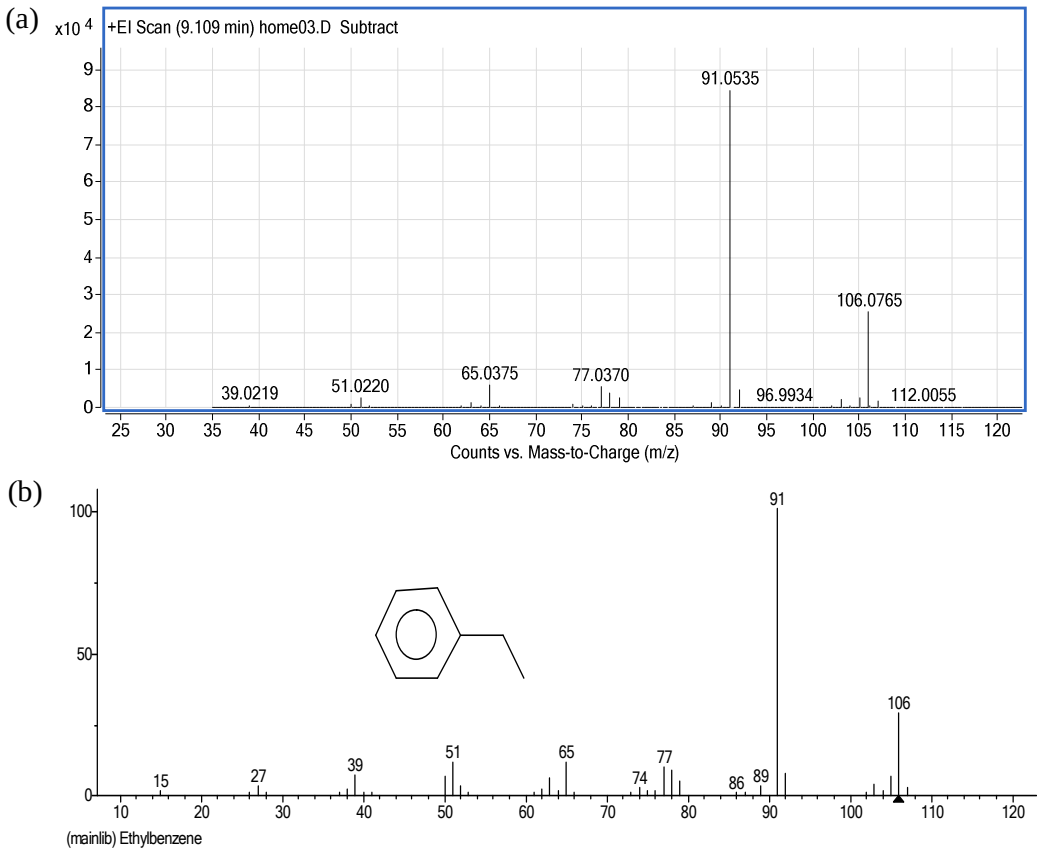


Figure A-21. Mass spectra of ethylbenzene (a) from Home 03 and (b) from NIST MS library.

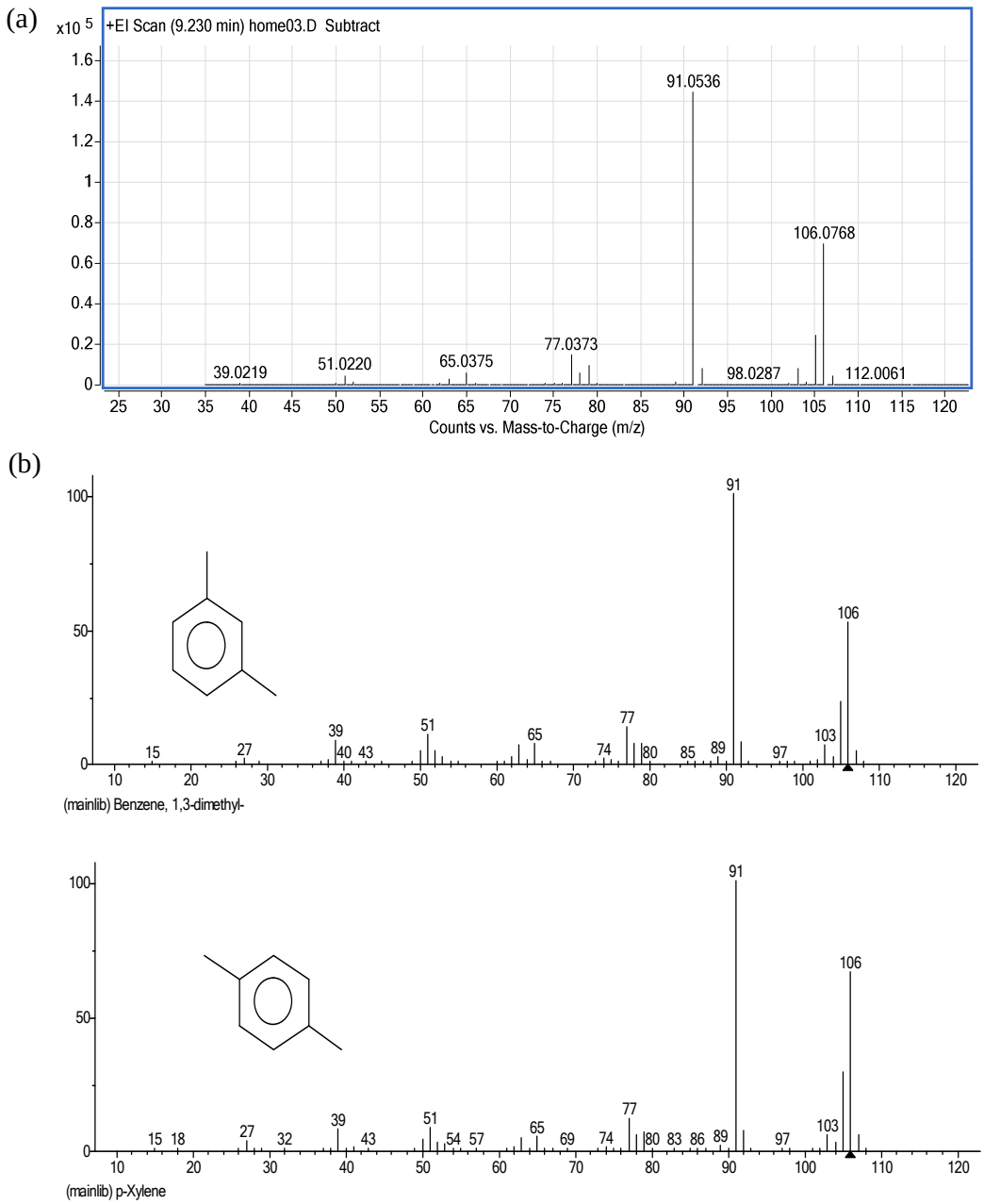


Figure A-22. Mass spectra of *m*+*p*-xylenes (a) from Home 03 and (b) from NIST MS library.

Appendix B

Consent form and Information Sheet for cVMS analysis in homes

Appendix B Consent form and Information Sheet for cVMS analysis in homes

CONSENT FORM

Indoor Air Sampling of Cyclic Volatile Methyl Siloxanes

Please initial

1. I confirm that I have read and understand the information sheet for the above study. I have had the opportunity to consider the information, ask questions and have had these answered satisfactorily. ☐

2. I understand that my participation is voluntary and that I am free to withdraw at any time, without giving any reason. ☐

3. I understand that any information given by me may be used in future reports, articles or presentations by the research team. ☐

4. I understand that my name will not appear in any reports, articles or presentations. ☐

5. I agree to take part in the above study. ☐

Name of Participant	Date	Signature

_____ _____ _____

Researcher Date Signature

Appendix B Consent form and Information Sheet for cVMS analysis in homes

INFORMATION SHEET

Indoor Air Sampling of Cyclic Volatile Methyl Siloxanes

Cyclic volatile methyl siloxanes (cVMS) are widely used in a variety of consumer products including fragrances, deodorants, cleaning products and lotions. cVMS are ideal for use as a solvent or matrix in these formulations because of their qualities of being inert, volatile, odourless and colourless. As a result, they are now produced commercially in high volumes. cVMS are however potentially bioaccumulative and persistent, with high octanol-water partition coefficient and with atmospheric oxidation half-lives of typically several days. There have been only limited observations or modelling of cVMS indoors and little is known about variability, exposure or distribution.

A passive sampling method has been developed and evaluated for the measurement of cVMS in indoor environments – this method was calibrated against an established active sampling method with good limit of detection values. Validation with the sampling of real homes would be the next step in the analysis of cVMS.

The aim of this work is to understand the ranges in the concentrations of cVMS detected in the homes of people in York, and to validate the passive sampling method that has been developed.

As a participant, you will be given a bottle containing sampling bag filled with ENV+ sorbents (as seen in Figure B-1). Carefully take out the sampling bag from the vial and hang the samplers using the attached paper clip in a chosen location in your home for a period of about 1-5 days (as discussed). After the sampling period, place the bag back into the vial and screw the cap on. The vial will be returned to the researcher after the sampling. Please take care not to touch the bags at any point.

Appendix B Consent form and Information Sheet for cVMS analysis in homes

Figure B-1. Sampling bag in vial.

You will be asked to provide information about the occupancy and ventilation in your homes, as well as the usage of consumer products (i.e. cleaning products, home fragrances, scented candles, hair sprays, deodorants, perfumes) over the period of sampling. Your responses will remain confidential and anonymous. Should you feel uncomfortable to provide the required details or if you change your mind, you can return the sampler and it will not be analysed. Prior to conducting the sampling, consent has to be obtained from all the residents in the house. All residents are required to sign the consent form before sampling can take place.

Appendix C Block diagram with code for Peltier device temperature control

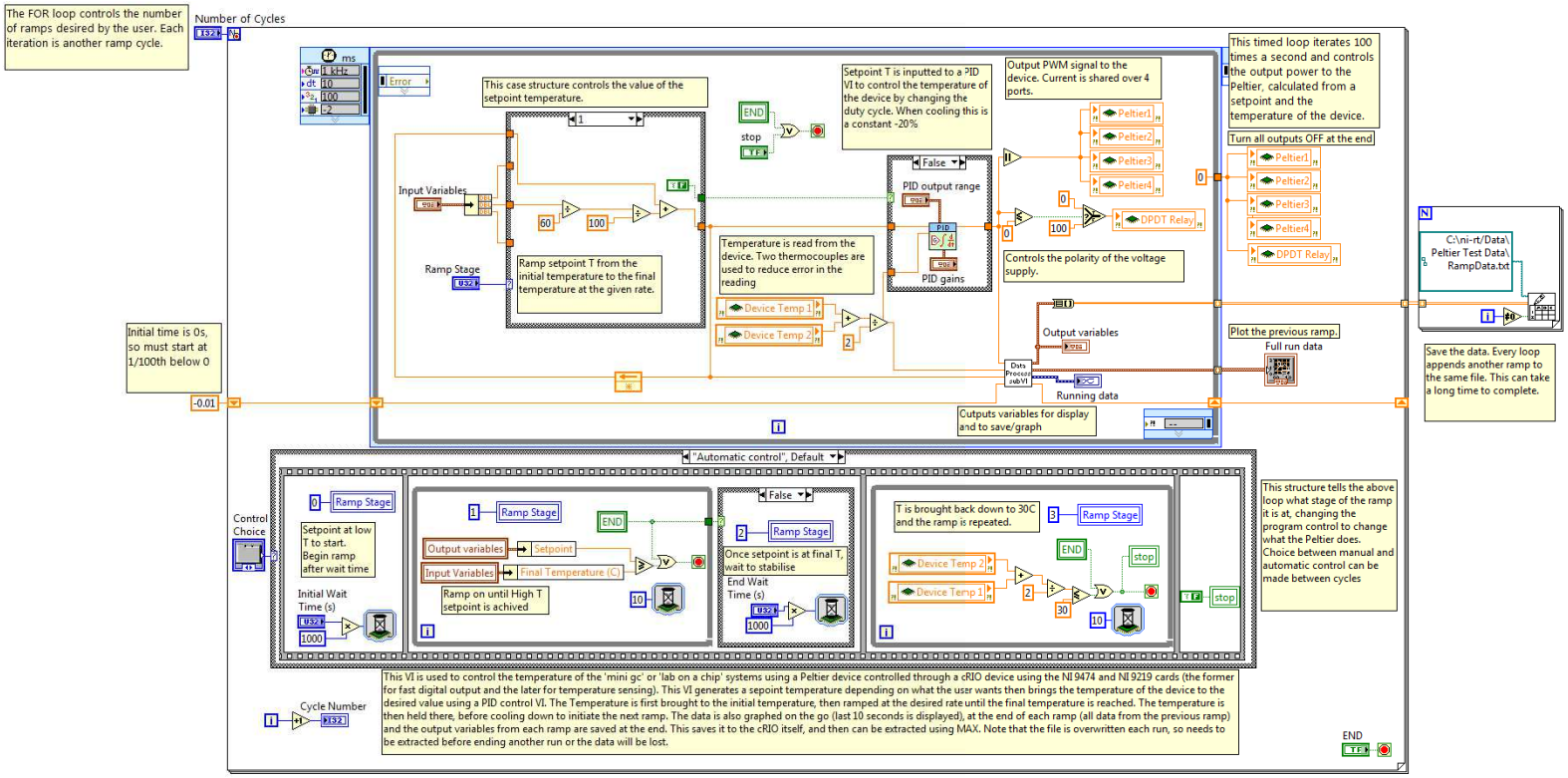


Figure C-1. Block diagram with code for Peltier device temperature control.

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